Department of Chemistry, The George Washington University, Washington 6, D.C.
and Goddard Space Flight Center, NASA, Greenbelt, Maryland.

Intramolecular Energy Transfer in Homogeneous and Mixed Lanthanide Complexes

(1) by: Nicolae Filipescu, Nelson McAvoy, Kishin Moorjani[1], Sven Bjorklund, Charles R. Hurt and Joel Zumoff.

Introduction

Rare earth ions incorporated in organic chelates by coordination through donor atoms such as oxygen or nitrogen, when excited in the region of light absorption associated primarily with the organic ligand, exhibit characteristic intra-4f parity forbidden fluorescence similar to the inorganic single crystal system. Direct excitation of the metal ion is not responsible for the line emission which, instead, is the result of an intramolecular energy transfer from the excited electronic states of the organic complex to the localized 4f energy levels of the chelated ion. The characteristic europium ion emission in homogeneous chelates (i.e., one ligand) has been previously investigated for both tris and tetrakis β-diketonates[2,3] and dipyridyl complexes.[4] (2,3,4)

We have reported[2a,b] on the effect of substituents attached directly to the β-diketonate chelate ring or more distant substituents on the electronic states of the organic ligand and the overall intramolecular energy migration in rare earth β-diketonates. The splitting of the lines and distribution of fluorescence among individual transitions originating at the $^5D_0$ and $^5D_1$ levels and terminating the ^7F ground multiplet of europium ion were found to be highly sensitive to changes in the organic part of the molecule. Both the symmetry and the intensity of the molecular field about the Eu^{3+} ion were significantly affected by

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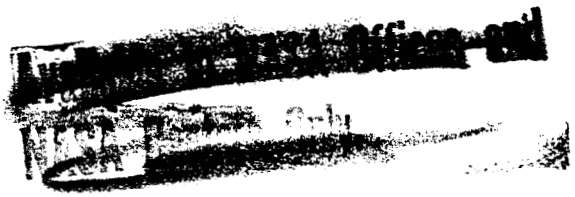


Author's Signatures:

Nicolae Filipescu

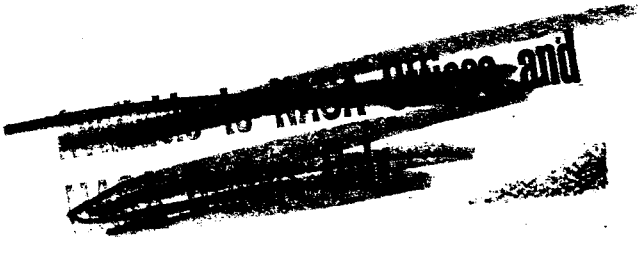
Nelson McAvoy

Kishin Moorjani

Sven Bjorklund

Charles R. Hurt

Joel Zumoff



ABSTRACT

The absorption, phosphorescence and phosphorescence excitation spectra of mixed Gd chelates reveal an interaction between the two types of ligand chromophores resulting in partial energy transfer from one to the other. The relatively small transfer efficiency is explained by the unfavorable orientation of the two chelating groups. In mixed Eu chelates, the ionic fluorescence is excited by light absorbed by either ligand. The fluorescence spectra of the tris, tris-aqua, tetrakis and mixed complexes are discussed in relation to molecular configuration. Preliminary results of the first order Stark effect calculations using distorted electrostatic models agree with the existence of a monomer-dimer mixture in the nominal tris chelates EuT_3 and EuD_3. This is confirmed by molecular weight determinations. The tetrakis and mixed Eu chelates are present as nonequivalent stereoisomers which explain the number of fluorescence lines observed.

modifications in ligand and consequently the transition probabilities inside the 4f shell are directly affected.

The present work is concerned with the energy migration processes in Eu and Gd complexes which have either only one type of ligand surrounding the lanthanide ion or two different chelating groups. Compared to a homogeneous chelate, a mixed system involves two sets of organic electronic excited states associated with the two different ligand chromophores and a more complex and asymmetric electric field about the rare earth ion induced by the surrounding atoms. This system has its own characteristics and is expected to be quite different from the one type ligand chelates. The two organic chromophores can be selected such that their absorption maxima are at different wavelengths and excited separately. The two ligands may interact with each other and with the europium ion to modify the overall intramolecular energy migration.

Experimental

Materials.- Methods previously described[2-4] have been employed to synthesize the following complexes: Tris chelates: Eu tris(theonyltrifluoroacetonate) (EuT_3), Eu tris(dibenzoylmethide) (EuD_3), Eu tris(benzoylacetonate) (EuB_3); Tetrakis chelates: Eu tetrakis(theonyltrifluoroacetonate)piperidinium (EuT_4P), Eu tetrakis(dibenzoylmethide)piperidinium (EuD_4P), Eu tetrakis(benzoylacetonate)piperidinium (EuB_4P); Bis chelates: Eu bis(dipyridyl)$Cl_3.2H_2O$ (EuDipy), Eu bis(1,10 phenanthroline)$Cl_3.3H_2O$ (EuPhen); Tris-aqua chelates: Eu tris(theonyltrifluoroacetonate)aqua (EuT_3A), Eu tris(dibenzoylmethide)aqua (EuD_3A), Eu tris(benzoylacetonate)aqua (EuB_3A); Mixed chelates: Eu tris(theonyltrifluoroacetonate)dipyridyl (EuT_3Dipy), Eu tris(theonyltrifluoroacetonate)phenanthroline

(EuT_3Phen), Eu tris(dibenzoylmethide)dipyridyl (EuD_3Dipy), Eu tris(dibenzoylmethide)phenanthroline (EuD_3Phen), Eu tris(benzoylacetonate)dipyridyl (EuB_3Dipy), Eu tris(benzoylacetonate)phenanthroline (EuB_3Phen); Gd chelates: Gd tris(theonyltrifluoroacetonate) (GdT_3), Gd tris(theonyltrifluoroacetonate)aqua (GdT_3A), Gd tris(theonyltrifluoroacetonate)dipyridyl (GdT_3Dipy), Gd tris(theonyltrifluoroacetonate)phenanthroline (GdT_3Phen).

The tris β-diketonates aqua were prepared in EtOH-H_2O from $EuCl_3$, β-diketone and NaOH[3a]. The tris compounds were obtained on heating the tris aqua chelates for 48 hours at 110°C in vacuum. The tetrakis β-diketonates were prepared in absolute EtOH adding piperidine to 4:1 mixture of ligand and $EuCl_3$. The procedures described by Melby et.al.[3a] and Bauer et.al.[3b] were employed for the preparation of mixed chelates. The chelates were repeatedly recrystallized from appropriate solvents and dried in vacuum. Analysis[3d] confirmed their composition.

Absorption Spectra.- Absorption in ultraviolet was determined with a Cary 15 spectrophotometer[5] in double beam mode at room temperature in methanol. (5) Ionic absorption spectra for Eu^{3+} in chelates were measured with the Cary 14[5] at room temperature and high concentrations (10^{-1}M) in 10 cm. path cells in dimethylformamide.

Fluorescence Spectra.- The fluorescence emission of the complexes was determined in microcrystalline powders at 77°K. Light from a 1000 watt, water cooled high pressure AH6 mercury lamp was filtered through a $NiSO_4$ water solution and a Corning CS7-54 filter and directed into a metal box constructed to prevent stray light from interferring with the measurements. A quartz dewar was positioned

in the box such that the excitation light would be focused on the sample which was sealed between quartz slides and immersed in liquid N_2 in the clear bottom part of the dewar. The fluorescence emission was directed through a Corning CS3-70 filter into the Cary 14 and detected by a R136 red-sensitive photomultiplier. The entrance slit to the Cary was adjusted manually to control the amount of light entering the monochromator. Dry air was caused to circulate inside the box to prevent possible frosting on the dewar and the 90° geometry was rigidly maintained. Spectra were recorded from 7500 to 5000Å and corrected for the different slit widths by extrapolating all the peaks to a common slit width (0.5mm) on relative intensity vs. slit width charts. The charts were determined by varying the slits for individual peaks and recording the output at each slit width. The spectra were also corrected for the spectral response of the photomultiplier tube. The areas under the peaks were calculated by considering the peaks as Gaussian structures and multiplying the relative intensities by the line width (in cm^{-1}) at the half power points. The percentage of the total fluorescence was determined for each line. The arithmetic work was done by a 7090 computer.

Organic Emission of Free Ligands and Gd Chelates, Phosphorescence and Fluorescence Excitation Spectra.- Organic fluorescence and phosphorescence of free ligands and Gd chelates were determined at liquid nitrogen temperature in
6) EPA with the Aminco-Bowman spectrophotofluorimeter[6] employing a 150 watt xenon lamp for excitation and an R-136 photomultiplier as detector. Freshly prepared samples were poured in the quartz tube and immersed in liquid nitrogen in the dewar supplied with the phosphoroscope attachment. The rotating shutter was not

used to detect the feeble organic fluorescence. The phosphorescence excitation spectra were measured using the same arrangement but scanning the excitation monochromator. The fluorescence excitation spectra (of Eu chelates) were run similarly, only the chelates were dissolved in dimethylformanide in a square 1 cm. cell in 90° geometry at room temperature. For these measurements, the concentrations used were such that the amount of light absorbed before the center of the 1 cm. cell would be less than 4.9% of the light at the wavelength of maximum absorption. No correction was needed, therefore, for the inner filter absorption by the solution. Both phosphorescence excitation and fluorescence excitation spectra were corrected for the spectral output of the Xe lamp and the corresponding spectral dispersion at various wavelengths for the slit widths
(7) employed.[7] The decay times of the organic phosphorescence were measured at 77°K in EPA using the time base recorder supplied by the manufacturer.[6]

Lifetime Measurements.- The excitation source employed was a "Strobotac"
(8) Type 1531-A electronic stroboscope[8] with a flash duration of approximately three microseconds. The light was focused into a black box after passing through a Corning CS7-60 filter. The dewar-sample arrangement was similar to fluorescence measurements. The fluorescence was directed through a Corning CS3-66 filter
(9) into a grating monochromator[9] at right angle to the excitation beam. The slits were adjusted to provide maximum resolution, and the detector used was an RCA 7265 S-20 photomultiplier. The photomultiplier signal was displayed on a Type 535A
(10) oscilloscope.[10]

RESULTS AND DISCUSSION

The absorption spectra of EuT_3, EuT_4P, EuDipy and mixture of T and Dipy are shown in Figure 1. A mixture of Dipy and T in a 1:3 ratio does not show any interaction between the two free ligands, the spectra of the mixture being a perfect addition of the separate individual absorbances. There is very little difference between the absorption spectra of Dipy (10^{-5}M) and $Eu(Dipy)2Cl_3.2H_2O$ (0.5×10^{-5}M) manifested in a slight bathochromic shift on complex formation of about 30Å for all three peaks and an insignificant increase in absorbance. A different picture is presented by the absorption of EuT_4P (10^{-5}M) when compared with the free ligand T (4×10^{-5}M). On chelate formation, the first $\pi \rightarrow \pi^*$ band at 3375Å increases markedly. This could be simply the result of complete conversion of the ketone-enol equilibrium in the free ligand to enolate anion in the chelate. There is ample evidence that aromatic β-diketones in solution are largely enolic and that the keto-enol equilibrium depends on the solvent polarity.[11] However, the presence of the CF_3 group on T increases the amount of ketone by lack of possible conjugation and negative inductive effects.[11c] The hyperchromism of the absorption band centered at 3425Å in dibenzoylmethane on chelate formation is much less significant than for theonyltrifluoroacetone because the first is essentially enolic in solution.

(Figure 1)

11)

The absorption spectrum of the mixed chelate EuT_3Dipy is quite different from an equivalent mixture of free ligands. The main $\pi \rightarrow \pi^*$ band is red shifted about 40Å and intensified to double the value of ε, whereas an opposite hypochromic effect is observed in the 2000-3500Å range associated with

absorption by the Dipy chromophore and $S_o \rightarrow S''$ in T. These differences are probably due to exciton interaction between the excited states of the two ligand chromophores in the mixed chelate. Such forms of interaction are
(12) believed to result in excitation delocalization[12] responsible for frequency
(13) shifts observed in dye aggregates and molecular crystals[13] and changes in
(14) intensity as found in associated molecules, double-chain polynucleotides[14],
(15) helical polypeptides and molecules containing two nonconjugated chromophores[15]. In addition, in mixed chelates the presence of the heavy and paramagnetic rare earth ion affects the interaction between the two ligand chromophores by changing
(16) the character and lifetime of their electronic levels.[2a, 16] These phenomena are best investigated in Gd chelates by measuring the phosphorescence of the system in the absence of Eu^{3+} chromophore. The results can be extended to the Eu complexes without any appreciable error because of the close atomic weight and paramagnetic characteristics of the two neighboring rare earth elements.

The emission and phosphorescence excitation spectra of three free ligands and their Gd chelates in rigid matrix at 77°K are shown in Figure 2, and the phosphorescence lifetimes are given in Table 1. A very weak organic fluorescence is observed in both free ligands and their Gd chelates, the values of $\phi_p/(\phi_p + \phi_f)$ being 0.96 for T and GdT_3, 0.86 for Dipy, and 0.88 for Phen respectively. No apparent change in $\phi_p/(\phi_p+\phi_f)$ occurs on complex formation. However, the phosphorescence decay times of the free ligands are modified drastically due to changes in both radiative and radiationless $T_1 \rightarrow S_o$ transition probability by the presence of the heavy and paramagnetic Gd ion.[16] This effect is essentially an enhanced spin-orbit admixing of the $T_1 \rightarrow S_o$ into the $S_1 \rightarrow S_o$ transition upon complexation

(Figure 2)

Table 1. Phosphorescence lifetimes of free ligands and Gd chelates in EPA at 77°K.

	Free ligand			GdT_3			GdT_3Dipy			GdT_3Phen		
	$\lambda_{exit.}$	$\lambda_{em.}$		$\lambda_{exit.}$	$\lambda_{em.}$		$\lambda_{exit.}$	$\lambda_{em.}$		$\lambda_{exit.}$	$\lambda_{em.}$	
Ligand	mμ	mμ	sec.	mμ	mμ	sec.	mμ	mμ	sec.	mμ	mμ	sec.
T	340	493	1.0	340	493	0.75	340 280	493 520	0.75 0.85	344	524	0.75
Dipy	285	448	0.7	-	-	-	280 235	456 426	2.4 5.0	-	-	-
Phen	265	450	3.5	-	-	-	-	-	-	280	420	0.55

with Gd for T and Phen ligands and an opposite decrease in admixture for Dipy inherent to its flexible structure. In general, the decay of the phosphorescence was found to be exponential; however, for Dipy the lifetime is a function of

(17) wavelength being shorter at longer wavelengths, which is not unusual.[17]

(18) The corrected[7,18] phosphorescence excitation spectra for the free ligands and GdT_3, displayed in Figure 2, are nearly proportional to the corresponding absorption spectra. This result is consistent with a constant quantum yield of emission anywhere in the absorption band. The analysis of the excitation and phosphorescence spectra of the mixed chelates in Figure 2 obtained by selective excitation and by isolating phosphorescence bands characteristic to one individual ligand-chromophore revealed the presence of intramolecular energy migration from one ligand to another. Thus phosphorescence from T is observed on excitation with light absorbed essentially by Dipy (234 mμ) or Phen (229 mμ) in GdT_3Dipy and GdT_3Phen respectively. Conversely, the characteristic Dipy phosphorescence (458 mμ) can be excited at wavelengths absorbed exclusively by T (335 mμ) in GdT_3Dipy and Phen. phosphorescence (457 mμ) is excited at 335 mμ in GdT_3Phen.

This process can take place by either dipole-dipole resonance or by exciton transfer, the overlap requirement of donor emission and acceptor absorption being satisfied for the singlet-singlet transfer from Dipy of Phen to T. At the same time, the overlap of the lowest triplets and their vibrationally excited states makes mutual triplet-triplet resonance transfer operational. Additional experiments (19) proved that no similar energy migration takes place in mixtures of free ligands[19] in which the two chromophores are situated more than 100Å apart. The observed energy transfer from one ligand to another in mixed chelates, although clearly shown in both excitation and phosphorescence spectra, has a smaller efficiency compared to other systems exhibiting this phenomenon.[15] This can be explained from the geometrical arrangement of the two chromophores in mixed chelates. Dipy (or Phen) in GdT_3Dipy (or GdT_3Phen) is situated in a plane that forms a 90° angle with the planes of two adjacent T groups and essentially in the same plane as the third (opposing) T group, or simply at right angles with each of the three T (20,21) groups.[20] Therefore, the orientation factor K,[21] being a function of the cosine of the angle between the donor and acceptor transition dipoles, has a very small value.

Replacing Gd with Eu in mixed chelates, the system becomes more complex containing three interacting chromophores. The corrected fluorescence (Eu^{3+}) excitation spectrum in mixed chelates in solution parallels closely the absorption spectrum proving that energy absorbed by either ligand is transferred to the complexed ion. The characteristic Eu fluorescence of the different complexes studied obtained on excitation with light absorbed by the organic part, is shown in Figures 3 to 6. In most previous work on Eu chelates[2,3], the 6300 to 7500Å spectral range corresponding to the $^5D_o \longrightarrow {}^7F_4$ transition has been neglected. Presently, we include these lines in the emission spectra of tris,

(Figures 3,4,5 & 6)

tris-aqua, and tetrakis, diketonates as well as Dipy, Phen, and mixed Eu chelates.

The fluorescence spectra were examined in microcrystalline powders to avoid the partial dissociation and additional coordination which take place on solvation.[22] Both ionic absorption (Figure 7) and emission have been employed to identify transitions from $^5D_0$ and $^5D_1$ levels to the ground ^7F multiplet. The absorption spectra at room temperature indicates that the $^7F_1$ and $^7F_2$ levels are sufficiently populated to cause absorption lines originating at these levels, which has also been reported by other investigators.[23] This data provides additional information to help identify the energetic location of the different energy levels and their splitting. The amount of molecular field splitting observed in chelates seems to be markedly higher than in ionic crystals ($LaCl_3$, ethyl sulfate, etc.). This implies that the field seen by the rare earth ion is stronger in chelate than in ionic crystals. Since the field strength depends on both the charge and the distance of the surrounding atoms from the rare earth ion, one conjectures that the nearest neighbors are closer in chelates, which is consistent with the partial covalent character of the Eu-O bond. Lifetime measurements of isolated fluorescence lines, expected to help in detailed recognition of the individual lines, were not very conclusive because of the very short life time of the $^5D_1$ level, comparable to the flash duration of our lamp, the weakness of certain lines and the limited resolution of the monochromator used. The observed groups of lines can be associated with certain transitions in the Eu ion: $^5D_0 \longrightarrow {}^7F_4$ appears in the 7200 - 6650 Å region, $^5D_0 \longrightarrow {}^7F_3$ in 6650 - 6440 Å, $^5D_0 \longrightarrow {}^7F_2$ in 6440 - 6030, $^5D_0 \longrightarrow {}^7F_1$ in 6030 - 5830 Å,

$^5D_0 \longrightarrow {}^7F_0$ around 5800 Å, and $^5D_1 \longrightarrow {}^7F_2$ and $^5D_1 \longrightarrow {}^7F_1$ overlap with the organic phosphorescence in the 5700 - 5200 Å region. These assignments are consistent with previous designations[3d,e]. The number of components observed for various identified levels apparently indicates that the symmetry of the tris-chelates is lower than octahedral and for the tetrakis and mixed chelates lower than tetragonal. (See below, however).

At least half of the complexes examined exhibited more than five components for the $^5D_0 \longrightarrow {}^7F_2$ transition, which is the maximum splitting of a level with $J = 2$ in a field of any symmetry. This is a clear indication that more than one emitting species is present. It has been suggested for the tetrakis diketonates[3d] that dissociation takes place in solution, where $EuKe_4^-$ is in equilibrium with $EuKe_3$ and Ke^-. However, our results indicate that even in the solid microcrystals exhibiting the correct elementar analysis for a homogeneous compound more than one species are present for all tris, tetrakis and mixed chelates. One possibility is that we have a mixture of different stereoisomers formed during synthesis which have nonequivalent molecular fields about the Eu ion and therefore the Stark components are found at different wavelengths. Another alternative is the existence of associated chelate molecules in which the enolate groups serve as bridges between two Eu ions. The existence of stereoisomers has been demonstrated for Gd^{3+} and Y^{3+} tris(acetylacetonates) by chromatographic separation of the optically active enantiomers[24]. X-ray studies have shown that the acetylacetonates of Co^{2+} and Ni^{2+} are tetrameric[25a] and trimeric[25b] respectively in crystalline form. In addition, an investigation of the absorption spectra of Eu tris(acetylacetonate) in different solvents has

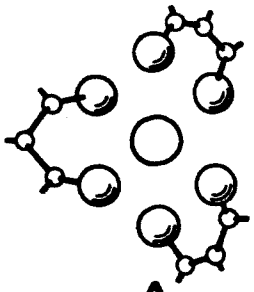
indicated the presence of both monomer and dimer[25c]. In chelates derived from unsymmetrical β-diketones and in mixed chelates, the number of possible stereoisomers is larger and considering the fact that the field of force responsible for the decomposition of the energy levels extends beyond the immediate neighborhood of the Eu ion[2a], the large number of Stark components observed is not to be unexpected.

The monomeric tris-chelates derived from symmetrically substituted β-diketones (model A, ex. EuD_3) can exist in two mirror image stereoisomers (enantiomers). These isomers will rotate the plane of polarized light in opposite directions but spectroscopically they are identical species. The maximum number of Stark components arising in a field of any symmetrical arrangement in Eu fluorescence are 9 for $^5D_o \longrightarrow {}^7F_4$, 7 for $^5D_o \longrightarrow {}^7F_3$, 5 for $^5D_o \longrightarrow {}^7F_2$, 3 for $^5D_o \longrightarrow {}^7F_1$ and one for $^5D_o \longrightarrow {}^7F_o$. The numbers of observed lines from crystalline EuD_3 for the same transitions are 9, 14, 5, 4 and 1 respectively. There must be two emitting species to account for these lines. One alternative is that in microcrystals the tris chelate is essentially dimeric and therefore can have two nonequivalent stereoisomers B and C. However these two stereoisomers differ only in the mutual orientation of the two pairs of end groups. These are relatively far from each other and therefore the two species will probably be essentially identical spectroscopic species.

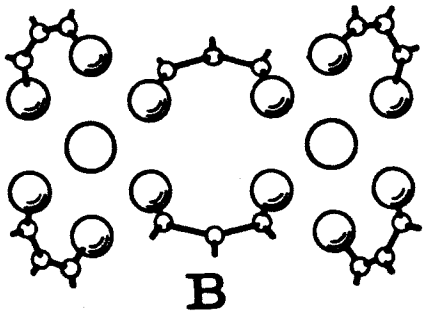
(Model A, B, C, D, and E)

Another possibility is that the powder consists of a monomer-dimer mixture. The general way of preparing tris-diketonates is to heat the hydrated [illegible] in vacuum. It is very possible that during this step a partial [illegible] of the monomeric tris-complex is converted to dimer, the final product

MODELS A, B, C, D, AND E



A



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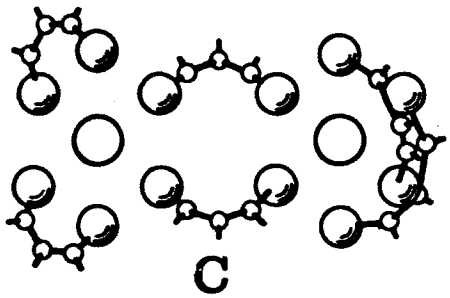

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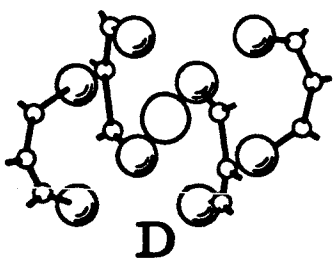
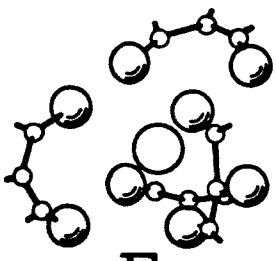


D



E

being a [illegible]-dimer mixture. Molecular weight determinations of nominally [illegible] confirmed this hypothesis. For example EuT_3 in benzene gave a number average molecular weight of 1050 which corresponds to 55 molecules of EuT_3 and 45 molecules of Eu_2T_6 in one hundred molecules in solution.[26] (26)

The solid tetrakis chelates are monomeric. They exhibit sharp melting points and their molecular weight in solution[26] is slightly less than calculated proving that dissociation takes place. The two possible stereoisomers of octacoordinated tetrakis β-diketonates do not have equivalent molecular field about the Eu ion and therefore two emitting species exist in the monomer to explain the number of lines observed. In some cases (EuB_3, EuB_3A, EuB_4P) the spectra can be interpreted as originating from only one species, which may show a preferential dimer formation for EuB_3 during preparation and equivalent stereoisomers for EuB_4P and EuB_3A, or simply a weaker Stark field resulting in small splitting with less possible resolution of the overlapping components.

We used the electrostatic models A, B (or C), D and E to calculate the expected splitting of the $^7F_1$ and $^7F_2$ levels. To account for the resonance delocalization of the negative charge along the enolate group, we considered the charge on the oxygen atoms as point charges displaced from the center of mass toward the inside of the chelate ring. We will refer to such models as distorted A, B, C, D and E. The first order Stark effect calculated from these models shows that the $^7F_1$ level should split into two components for distorted A, B and D, and three for E respectively. In a mixture of A and B one should observe four different lines for the $^5D_0 \rightarrow {}^7F_1$ transition. In a

D and E mixture one should also observe four levels because the secular determinants of the two distorted tetrakis isomers have a common solution.

In light of these calculations the four components of the $^7F_1$ level observed in the fluorescence spectrum of EuD_4P can be assigned as belonging to the distorted D (505 and 289 cm^{-1}) and distorted E (446 and 361 cm^{-1}).

The $^5D_0 \longrightarrow {}^7F_2$ transition should generate 8 components for a A and B (or C) mixture and the same number for a D and E mixture, which is what we actually observe for EuD_3 and EuD_4P. Using the mentioned distorted models we found for the "crystal field" parameters[27] $\langle A_2^0 \rangle$ the values of -360 and -140 cm^{-1} for species D and E respectively in EuD_4P[28].

The relative intensities of the individual fluorescence lines expressed as percentage of total Eu ion emission are listed in Table II. To calculate these values, the fluorescence spectra were corrected for slit width and photomultiplier response (see Experimental). The arrows employed for the $^5D_0 \longrightarrow {}^7F_4$, $^5D_0 \longrightarrow {}^7F_3$ and $^5D_1 \longrightarrow {}^7F_2$ transitions designate "band with structure" with approximate limits at the top and bottom of the group. Only ω_{max} of clearly defined peaks is given[29]. This type of characterization was not needed for the $^5D_0 \longrightarrow {}^7F_2$ and $^5D_0 \longrightarrow {}^7F_1$ transitions which give relatively clear sets of lines. The variation in relative intensity of specific transitions on changing the organic part of the chelate molecule is impressive. Some general observations can be made. The tris and the trisaqua complexes in each of the three β-diketonates investigated are fairly close in fluorescence distribution among specific $^5D \longrightarrow {}^7F$ transitions. The relative intensity of the $^5D_0 \longrightarrow {}^7F_4$ group of lines is highest for the dibenzoylmethides, lowest for benzoylacetonates and intermediate for thenoyltrifluoroacetonates. On going from a tris to a tetrakis β-diketonate the effects vary from one type of ligand to another. In EuT_4P the

Table II. Relative Intensities of Individual Fluorescence Lines

TRANSITION	EuT_3 ω_{max} cm^{-1}	%	EuT_3A ω_{max} cm^{-1}	%	EuT_4P ω_{max} cm^{-1}	%	EuT_3 Dipy ω_{max} cm^{-1}	%	EuT_3 Phen ω_{max} cm^{-1}	%	EuD_3 ω_{max} cm^{-1}	%	EuD_3A ω_{max} cm^{-1}	%	EuD_4P ω_{max} cm^{-1}	%	EuD_3 Dipy ω_{max} cm^{-1}	%	EuD_3 Phen ω_{max} cm^{-1}	%	EuB_3 ω_{max} cm^{-1}	%	EuB_3A ω_{max} cm^{-1}	%	EuB_4P ω_{max} cm^{-1}	%	EuB_3 Dipy ω_{max} cm^{-1}	%	EuB_3 Phen ω_{max} cm^{-1}	%	EuDipy ω_{max} cm^{-1}	%	EuPhen ω_{max} cm^{-1}	%
$^5D_0 \rightarrow {}^7F_4$	14050		14050		14100		14050		14000		14050		14050		14050		14050		14050		14050		14080		14050		14050		14050		14050		14050	
	↑	3.5	↑	3.1	↑	0.6	↑	6.8	↑	2.2	↑	3.1	↑	5.7	↑	8.3	↑	6.5	↑	1.9	↕	5.9	↕	5.8	↑	1.1	↑	3.4	↑	2.0	↑	0.8	↑	19.6
	14237	4.9	14239	4.2	14282	6.0	14235	6.2	14011	3.9	14290	22.5	14296	18.9	14251	15.3	14231	8.6	14198	5.3	15000		15000		14241	18.3	14202	15.2	14190	12.0	14188	5.0	14282	15.1
	14324	6.2	14333	6.1	14362	5.5	14327	4.9	14215	4.8	14654	1.9	14656	1.5	↓	14.2	14524	4.0	↓	5.1					↓	1.6	14245	11.4	↓	2.4	14271	8.3	14372	7.0
	↓	3.6	↓	1.1	14684	1.2	14400	1.8	14245	9.9	14732	0.6	14885	1.1	15050		14932	0.7	14265	6.0					15000		↓	4.6	14500		14324	6.1	14579	6.5
	15000		15000		14874	2.4	14545	3.2	14388	2.6	14767	0.6	14966	1.2			15020	0.5	15100								15000				14324	6.1	14579	6.5
					15028	0.8	14712	1.6	14961	2.7	14903	1.0	↓	0.3			↓	5.8													14552	2.8	↓	9.2
					↓	0.2	14868	0.9	14876	0.9	14957	1.6	15000				15100														14600		0.3	14650	
					15100		15020	0.5	15024	0.5	↓	0.5																						
							↓	2.0	↓	3.3	15000																							
							15100		15100																									
$^5D_0 \rightarrow {}^7F_3$	15180		15180		15180		15100		15220		15276	2.2	15286	5.0	15335	3.9	15265	1.2	15304	2.1	15200		15200		15250		15200		15200		15200		15200	
	↑		↑		↑		↑	0.2	↑	0.1	15326	1.6	15392	2.6			15316	1.4	15382	2.1	↑		↑		↑		↑	0.7	↑	1.6	↑		↑	
	15344	2.6	15366	1.2	15221	1.9	15179	0.1	15344	2.9	15389	1.6					15361	3.2			15330	1.7	15232	1.7	15330	2.8	15270	1.3	15400		15361	0.8	15356	1.4
	↓		↓		15337	7.4	15335	3.6	↓	0.1											↓		↓			15330	2.9						
	15480		15480		15415	4.8	↓	0.3	15550												15480		15400		15400		↓	1.1			15450		15450	
					↓		15550																				15500							
					15480																													
$^5D_0 \rightarrow {}^7F_2$	16085	8.8	16085	8.0	15823	0.7	15783	2.0	15798	1.5	15815	0.7	15865	3.2	15840	2.1	15630	0.9	15637	0.5	16210	18.4	16054	2.9	15820	1.0	15860	2.0	15850	0.7	16077	8.6	16077	2.8
	16134	10.5	16137	9.9	15858	1.2	15835	1.5	15880	1.5	15868	2.3	15956	3.3	15990	3.9	15848	1.6	15868	2.3	16287	21.2	16210	15.4	16018	3.2	15872	2.0	16013	6.1	16142	23.3	16152	5.6
	16207	22.8	16205	13.2	15941	3.2	15964	3.2	15982	2.8	15949	2.7	16265	17.8	16119	1.2	15990	4.2	15990	8.6	16329	32.8	16279	22.6	16192	7.5	16173	4.3	16119	4.9	16194	17.5	16205	4.4
	16265	12.6	16263	24.0	16132	4.1	16171	9.7	16139	7.5	16020	1.2	16324	13.5	16204	4.9	16131	7.5	16137	21.2	16385	11.7	16326	24.7	16313	25.6	16268	7.1	16205	7.3	16284	11.0	16279	3.7
	16356	10.4	16356	13.9	16326	19.1	16194	11.0	16197	11.4	16265	9.3	16466	1.8	16210	8.8	16181	21.1	16181	11.8			16385	15.2	16332	24.7	16281	18.4	16310	26.7	16326	10.3	16316	11.0
					16356	16.0	16303	7.8	16231	5.8	16321	12.3	16567	1.0	16313	7.9	16324	8.6	16321	11.1							16377	12.3	16356	26.1				
					16589	1.3	16332	7.4	16345	17.8	16461	1.7			16342	8.2	16367	9.1	16367	5.4							16556	1.5						
							16551	1.3			16559	0.9			16551	1.3	16545	1.0	16567	0.6														
$^5D_0 \rightarrow {}^7F_1$	16778	4.9	16787	3.6	16793	7.3	16784	4.3	16753	3.9	16818	9.7	16824	5.6	16736	1.9	16734	3.6	16728	4.5	16815	4.0	16810	5.3	16810	0.4	16734	1.8	16903	2.4	16812	1.7	16807	3.4
	16892	2.9	16882	4.2	16866	8.2	16886	6.4	16895	5.5	16835	10.2	16841	5.7	16795	6.5	16889	3.2	16880	4.2	16978	2.4	16964	3.3	16883	5.4	16869	5.1	16923	5.5	16898	2.8	16866	3.6
	16969	2.3	16969	3.6	17129	6.2	16909	6.8	16955	5.2	16966	3.7	16978	2.2	16880	4.0	16958	4.1	17007	1.9					16932	5.8	16912	2.9	17007	0.5			16952	3.5
							17047	2.2			16998	5.0	17007	5.1	16943	4.3			17024	1.6													17132	0.5
							17106	4.0																										
$^5D_0 \rightarrow {}^7F_0$	17259	2.0	17250	2.5	17265	0.5	17235	0.6	17250	1.8	17256	1.1	17250	1.3	17241	1.1	17241	1.7	17254	2.9	17247	1.6	17241	2.2	17247	1.0	17241	0.8	17241	1.8	17247	0.4	17244	1.6
$^5D_1 \rightarrow {}^7F_2$	17730		17750		17730		17752	0.6	17730		17715	0.2	17670		17745	0.2	17727	0.3	17765	0.1	17670		17670		17670		17742	0.2	17943	0.1	18041	0.1	18016	0.3
	↑		↑		↑	0.1	17934	0.1	↑		17937	0.1	↕	1.1	17837	0.2	17892	0.5	17895	0.1	↕	0.1	↕	0.4	↕	0.4	18021	0.2						
	17920	0.3	18018	0.4	18300		18064	0.1	17931	0.5	18093	0.3	18300		18077	0.2	18086	0.3	18103	0.1	18300		18300		18300									
	↓		↓						↓																									
	18300		18300						18300																									
$^5D_1 \rightarrow {}^7F_1$	18518	0.9	18518	0.6	18574	0.2	18500	0.1	18518	0.3	18584	0.8	18587	1.4	18666	1.4	18488	0.4	18505	0.2	18692	0.3	18580	0.6	18660	0.2	18608	0.7	18625	0.1	18646	0.2	18692	0.7
	18709	0.9	18702	0.7	18797	0.2	18625	0.3	18685	0.5	18751	0.4	18762	0.8			18685	0.5	18706	0.3														

*Percentage Total Emission

$^5D_o \longrightarrow {}^7F_4$ transition remains about the same, whereas the $^5D_o \longrightarrow {}^7F_3$ and $^5D_o \longrightarrow {}^7F_1$ groups increase substantially at the expense of the $^5D_o \longrightarrow {}^7F_2$ lines. EuD_4P exhibits an opposite trend: higher intensity for the $^5D_o \longrightarrow {}^7F_4$ group and decreased relative contribution from $^5D_o \longrightarrow {}^7F_3$ and $^5D_o \longrightarrow {}^7F_1$. In EuB_4P a sizable decrease in relative intensity is observed for the $^5D_o \longrightarrow {}^7F_2$ lines with corresponding increase in the $^5D_o \longrightarrow {}^7F_4$, $^5D_o \longrightarrow {}^7F_3$ and $^5D_o \longrightarrow {}^7F_1$ groups. The formation of mixed diketonates with Dipy or Phen also determines significant changes in relative distribution. Compared to EuT_3, the mixed EuT_3Dipy and EuT_3Phen complexes show marked increase in the $^5D_o \longrightarrow {}^7F_4$ lines at the expense of the $^5D_o \longrightarrow {}^7F_2$. On the contrary EuD_3Dipy and EuD_3Phen exhibit enhanced $^5D_o \longrightarrow {}^7F_2$ contribution with weakening of the $^5D_o \longrightarrow {}^7F_4$ group (compared to EuD_3). The effects on EuB_3 are opposite for EuB_3Dipy and EuB_3Phen. The relative intensities of the $^5D_o \longrightarrow {}^7F_4$ and $^5D_o \longrightarrow {}^7F_2$ lines in EuDipy and EuPhen are completely reversed. One could extend this discussion to statistical weight of individual lines inside a certain $^5D \longrightarrow {}^7F$ group. However, at the present ime, these are merely observations and no prediction can be made with respect to energy distribution among individual transitions as function of molecular structure or nature of ligands. To be able of such predictions, an accurate description of the molecular field is necessary and a rigorous interaction of the 4f electrons must be taken into consideration, in addition to specific details of the wave functions which are not known. Approximate calculations are also possible and some effort is devoted presently in this direction.

The relative (total) fluorescence intensities of different microcrystalline Eu chelates [illegible] are compared in Table III. These figures represent the

sum of the areas under all fluorescence peaks after correction for slit width and detector response, on a wave number chart, normalized arbitrarily for EuT_3=0.2. Assuming that all chelates absorb about the same number of quanta in the experimental arrangement used, the numbers in Table III should be approximately proportional to the absolute quantum efficiency, which is not known for chelates in powders.

Table III. Relative quantum efficiencies of Eu chelates (powders) at 77°K.

EuT_3	0.20	EuT_3A	0.28	EuT_4P	0.42	EuT_3Dipy	0.90	EuT_3Phen	0.46
EuD_3	0.60	EuD_3A	0.27	EuD_4P	0.43	EuD_3Dipy	0.38	EuD_3Phen	0.29
EuB_3	0.31	EuB_3A	0.13	EuB_4P	0.15	EuB_3Dipy	0.27	EuB_4Phen	0.10
						EuDipy	0.42	EuPhen	0.23

Chelates containing phenanthroline are consistently poorer emittors than their dipyridyl analogs. The variation in relative quantum efficiency does not follow a regular pattern for the three different β-diketonates is not unexpected because the presence of different species (stereoisomers or monomer-dimer mixtures), the intersystemcrossing, and the Ligand→Eu^{3+} transfer efficiency are all dependent on the substituents attached to the enolate ring. The data obtained in powders cannot be extrapolated to solutions where dissociation, additional coordination, and solvent quenching will be present.

The first Eu chelate found to exhibit laser activity in solution was EuB_4P[30]. Subsequently a few more have been added to the list, all belonging to the tetrakis β-diketonate species. It has been puzzling to find out that chelates with equivalent or higher quantum efficiency did not perform as lasers.

The lifetime of the ^5D_o state does not vary critically, remaining in the millisecond range for most chelates in solution. But the presence of a unique emitting species, a relatively high quantum efficiency, and a proper fluorescence distribution among individual lines are also essential for lasing. The existence of two or more species in solution will lead to undesired competition. Another loss of effective pumping energy is found in transitions originating at the ^5D_o level and terminating at ^7F levels other than $^7F_2$, and these are by no means insignificant. Both empirical and theoretical correlations of these factors with molecular structure are important in designing the most adequate systems for liquid chelate lasers.

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FIGURE 1. Absorption spectra of free ligands and their Eu chelates in CH_3OH. (A) T 3 x 10^{-5}M; (B) Dipy 10^{-5}M; (C) T 3 x 10^{-5}M + Dipy 10^{-5}M; (D) EuT_3Dipy 10^{-5}M; (E) EuT_4P 10^{-5}M.

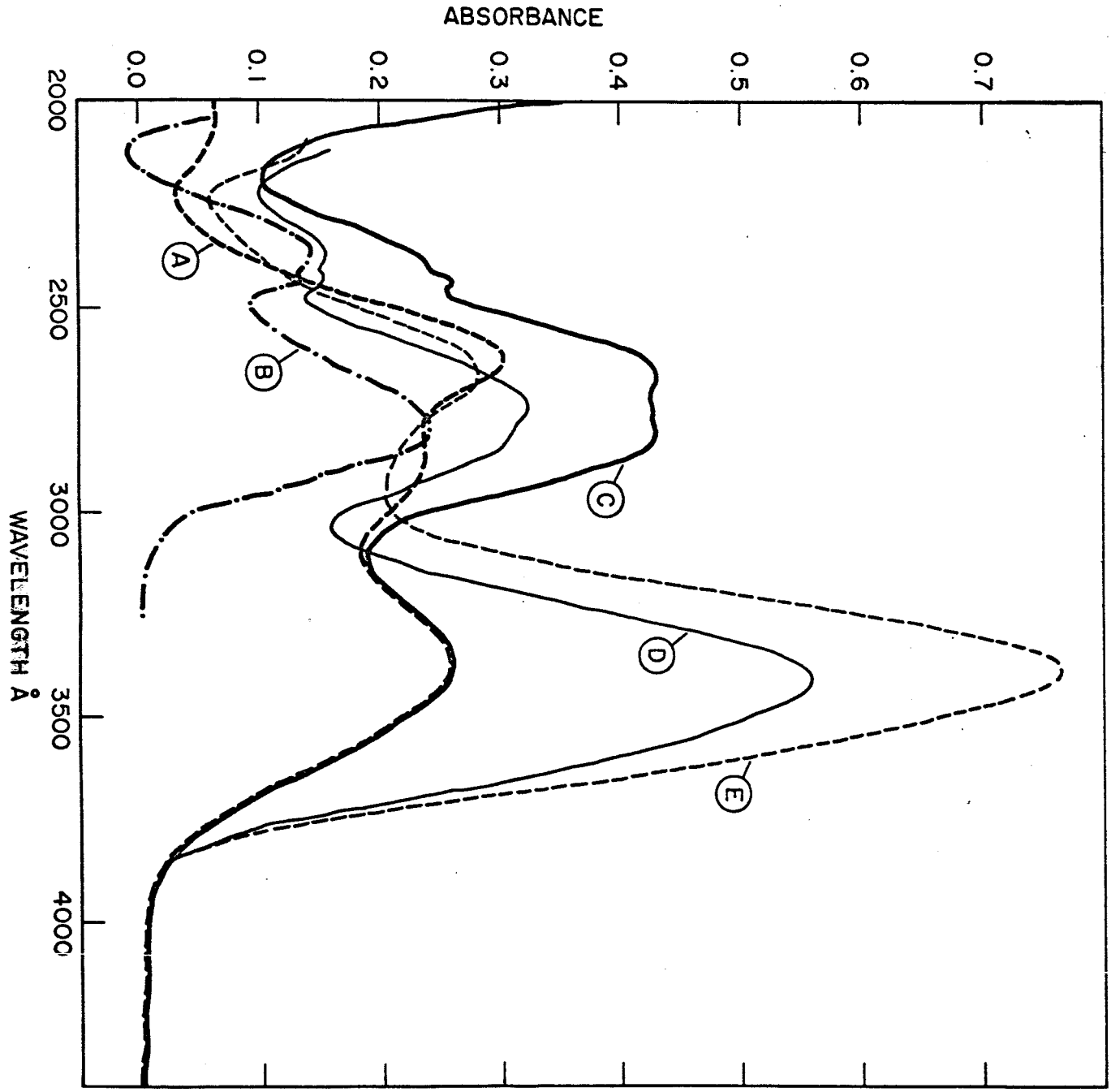


FIGURE 2 (a) Phosphorescence spectra of Dipy 10^{-5}M in EPA at 77°K: (A) Excitation of phosphorescence (456 mμ), (B) phosphorescence excited at 281 mμ.

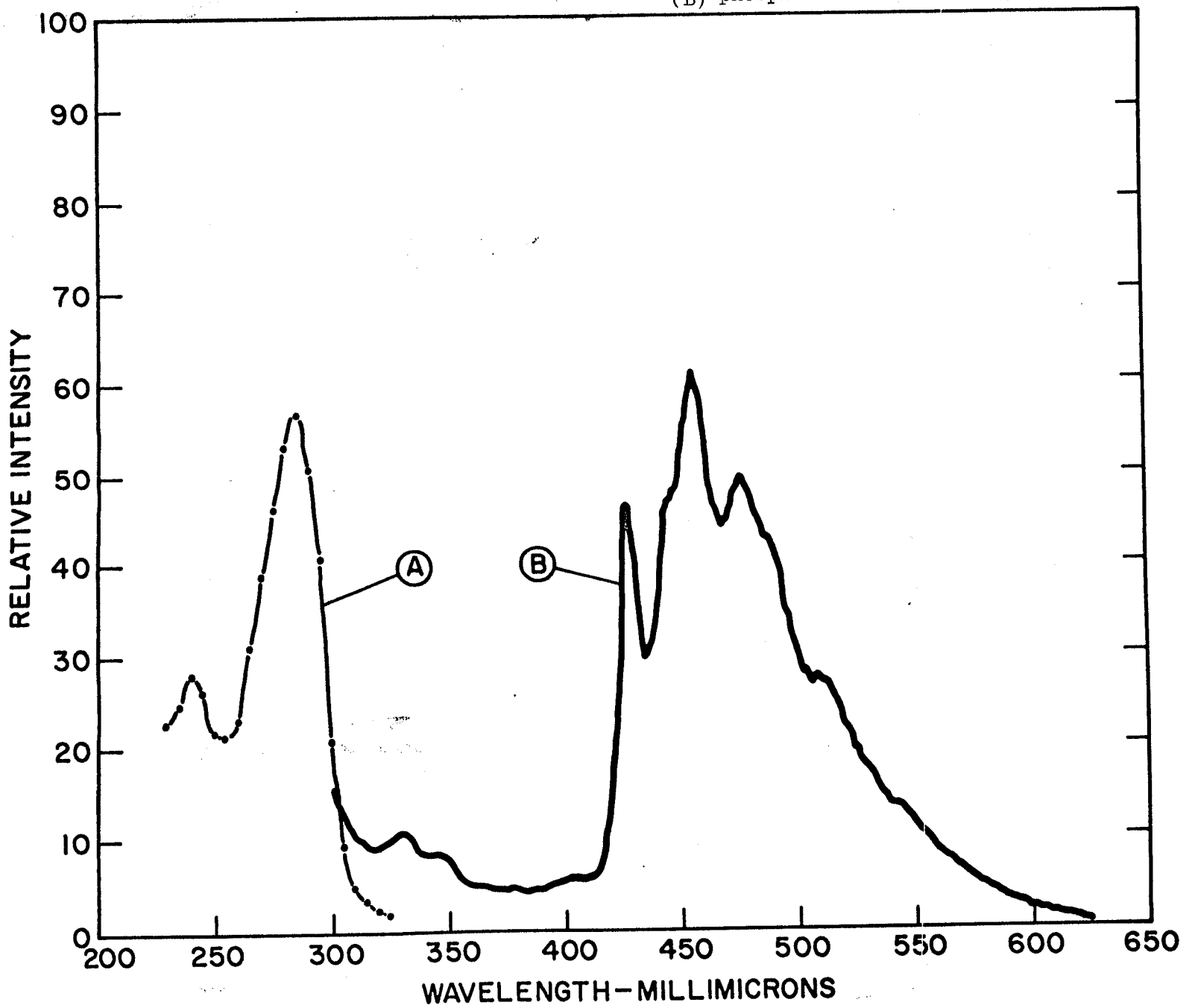


FIGURE 2 (b) Phosphorescence spectra of Phen 10^{-5}M in EPA at 77°K: (A) Phosphorescence excited at 270 mμ, (B) Excitation of phosphorescence (454 mμ).

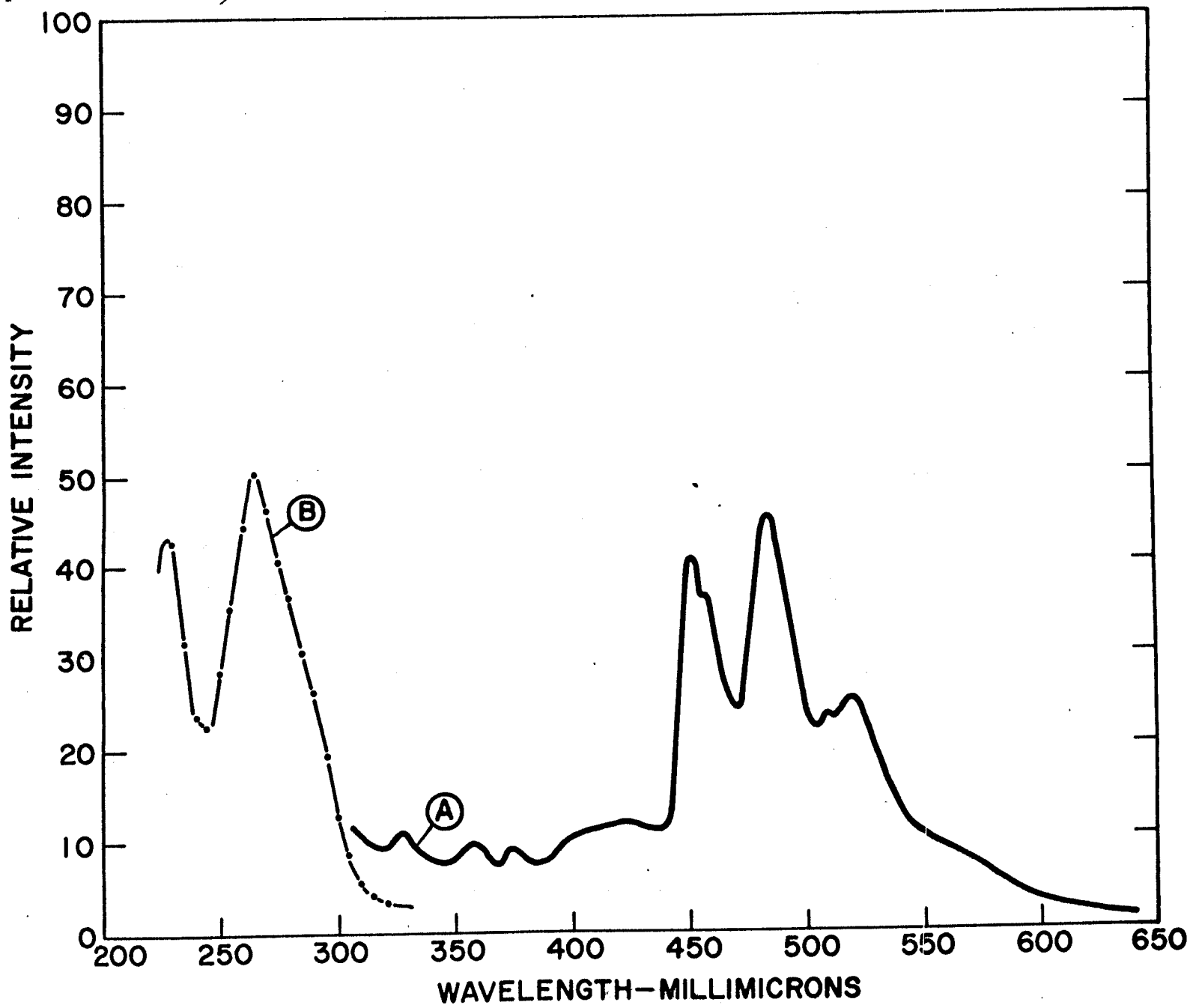


FIGURE 2 (c) Phosphorescence spectra of GdT_3 10^{-5}M in EPA at 77°K: (A) emission excited at 340 mμ, (B) phosphorescence excited at 285 mμ, (C) excitation of phosphorescence at 420 mμ, (D) same as (B) with higher amplifier sensitivity.

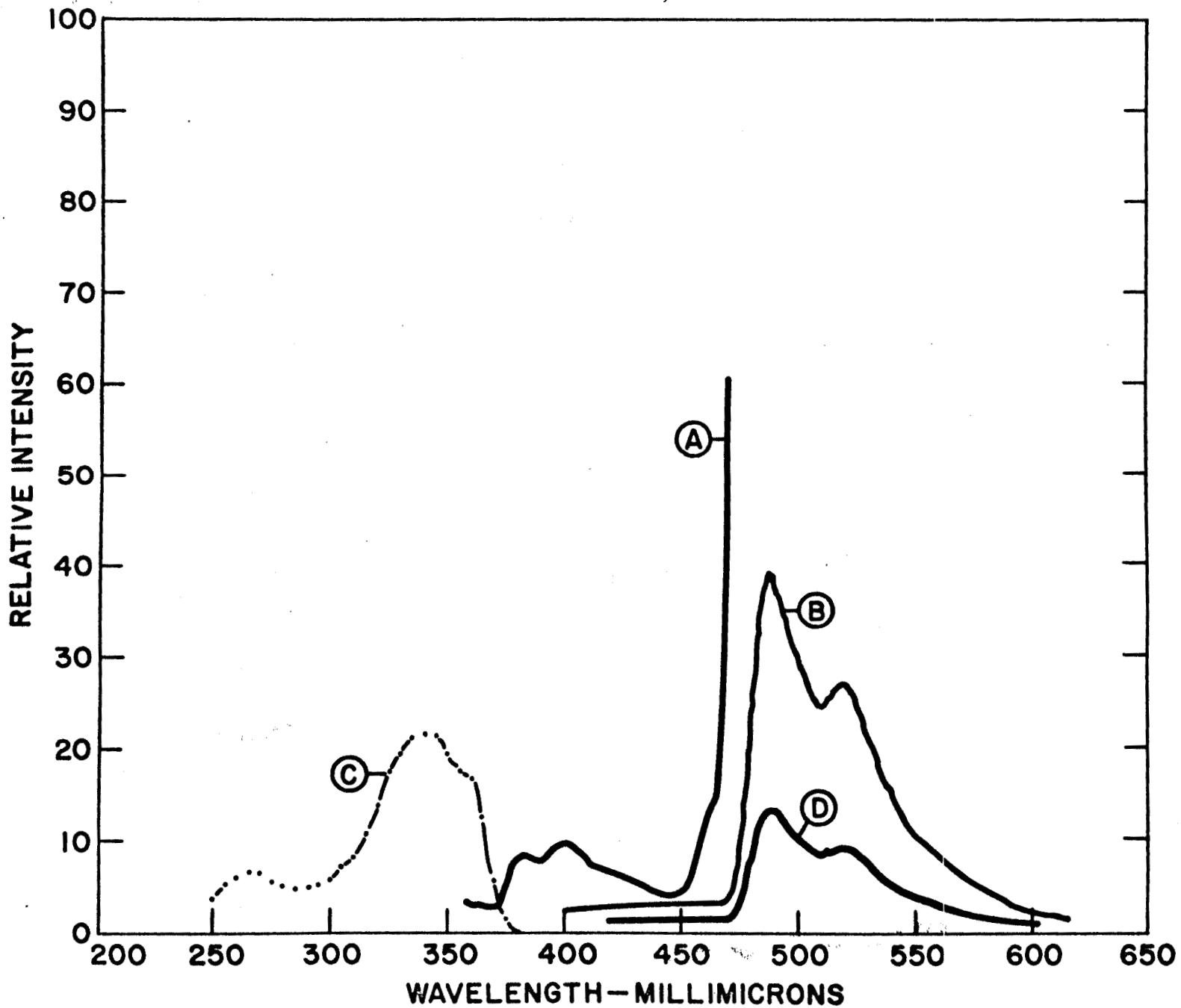
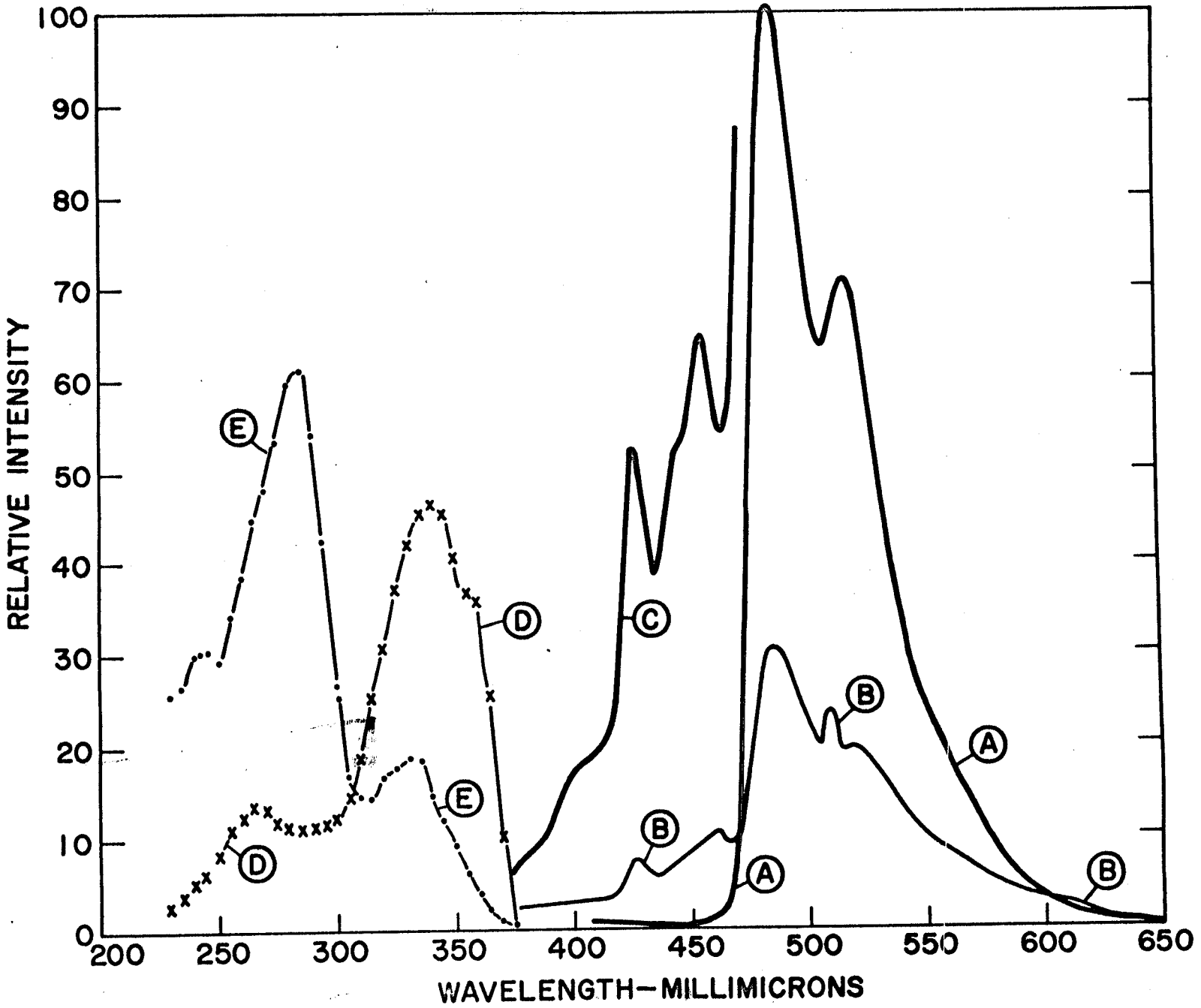


FIGURE 2 (d) Phosphorescence spectra of GdT_3Dipy 10^{-5}M in EPA at 77°K: (A) phosphorescence excited at 345 mμ, (B) phosphorescence excited at 234 mμ, (C) phosphorescence excited at 280 mμ, (D) excitation of phosphorescence(489 mμ



(E) excitation of phosphorescence at 426 mμ.

FIGURE 2 (e) Phosphorescence spectra of GdT_3Phen 10^{-5}M in EPA at 77°K: (A) excitation of the 456 mμ peak, (B) excitation of phosphorescence (490 mμ), (C) phosphorescence excited at 229 mμ, (D) phosphorescence excited at 345 mμ, (E) phosphorescence excited at 265 mμ.

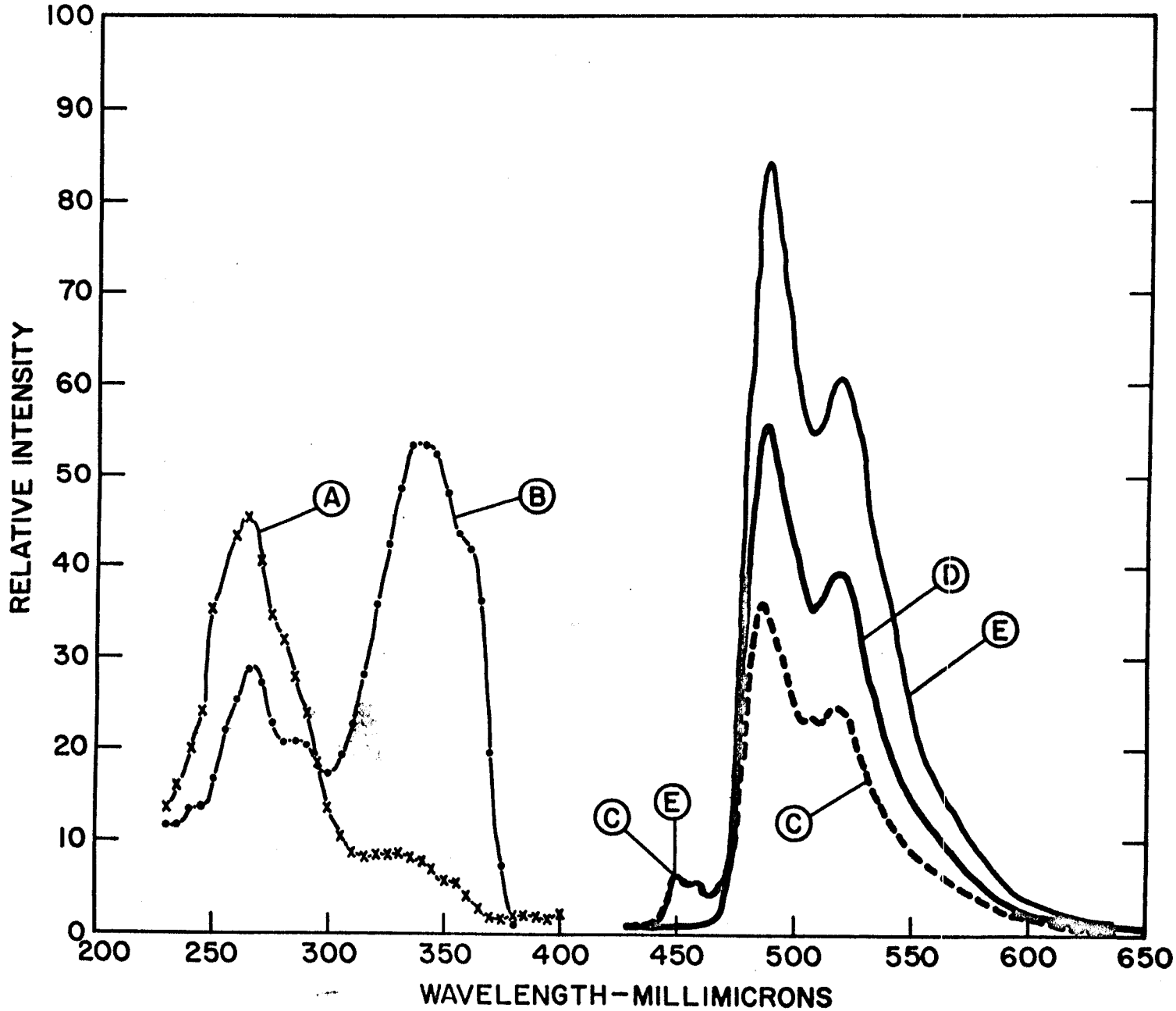


Figure 3 (a) Fluorescence spectra of microcrystalline Eu chelates at 77°K. (a). EuT_3.

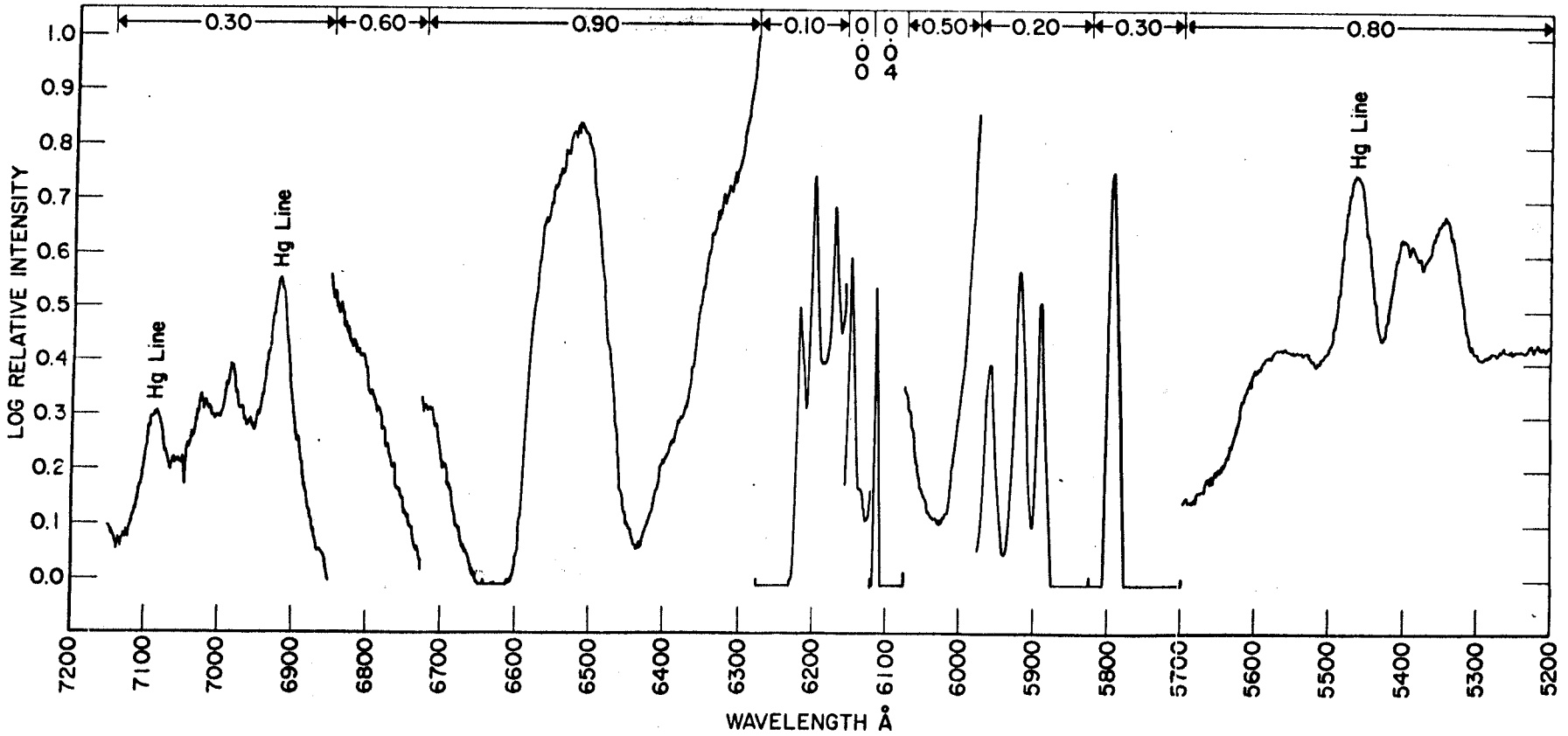


FIGURE 3 (b). Fluorescence Spectra of Microcrystalline Eu chelates at 77°K. (b) EuT_3A

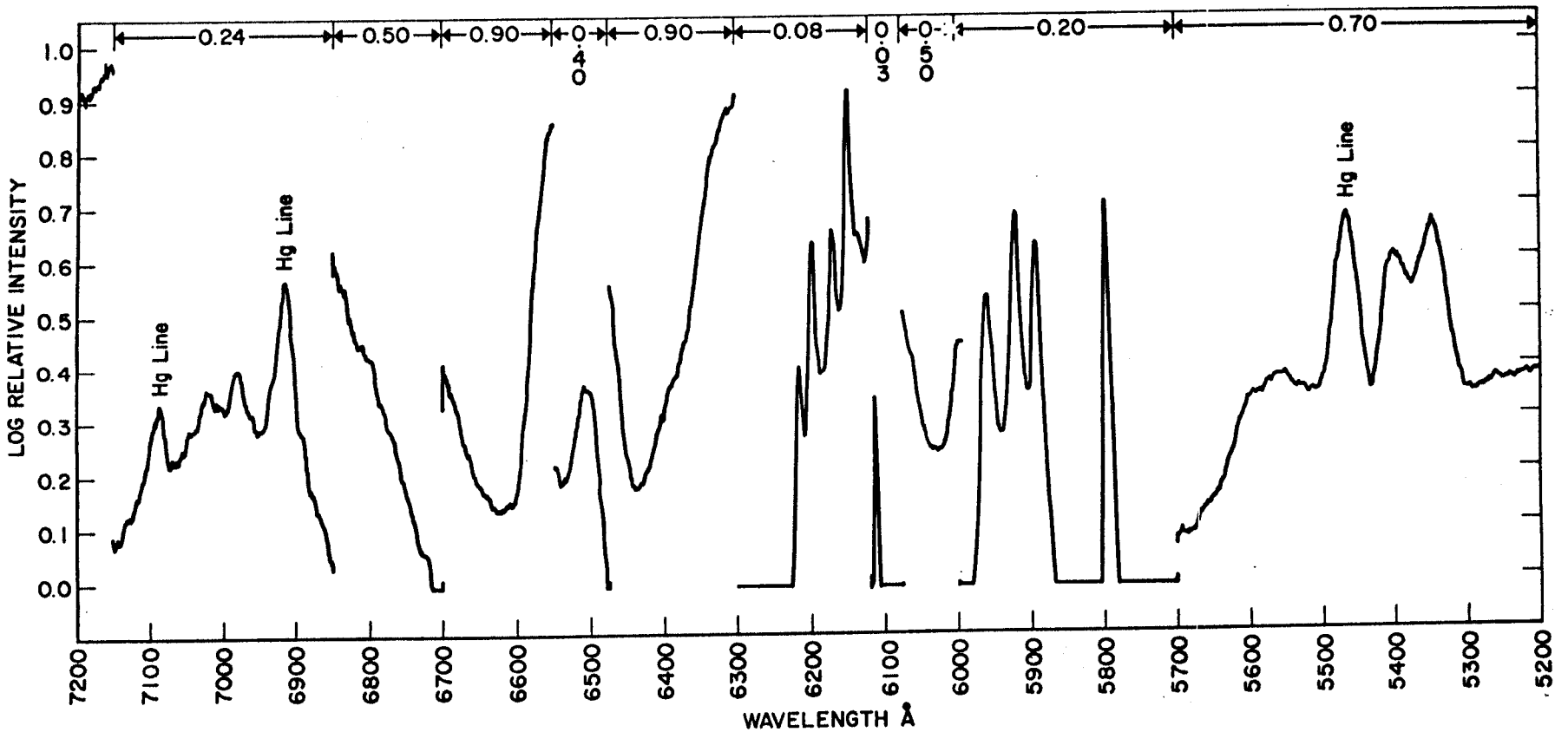


FIGURE 3 (c). Fluorescence spectra of microcrystalline Eu chelates at 77°K. (c) EuT_4P

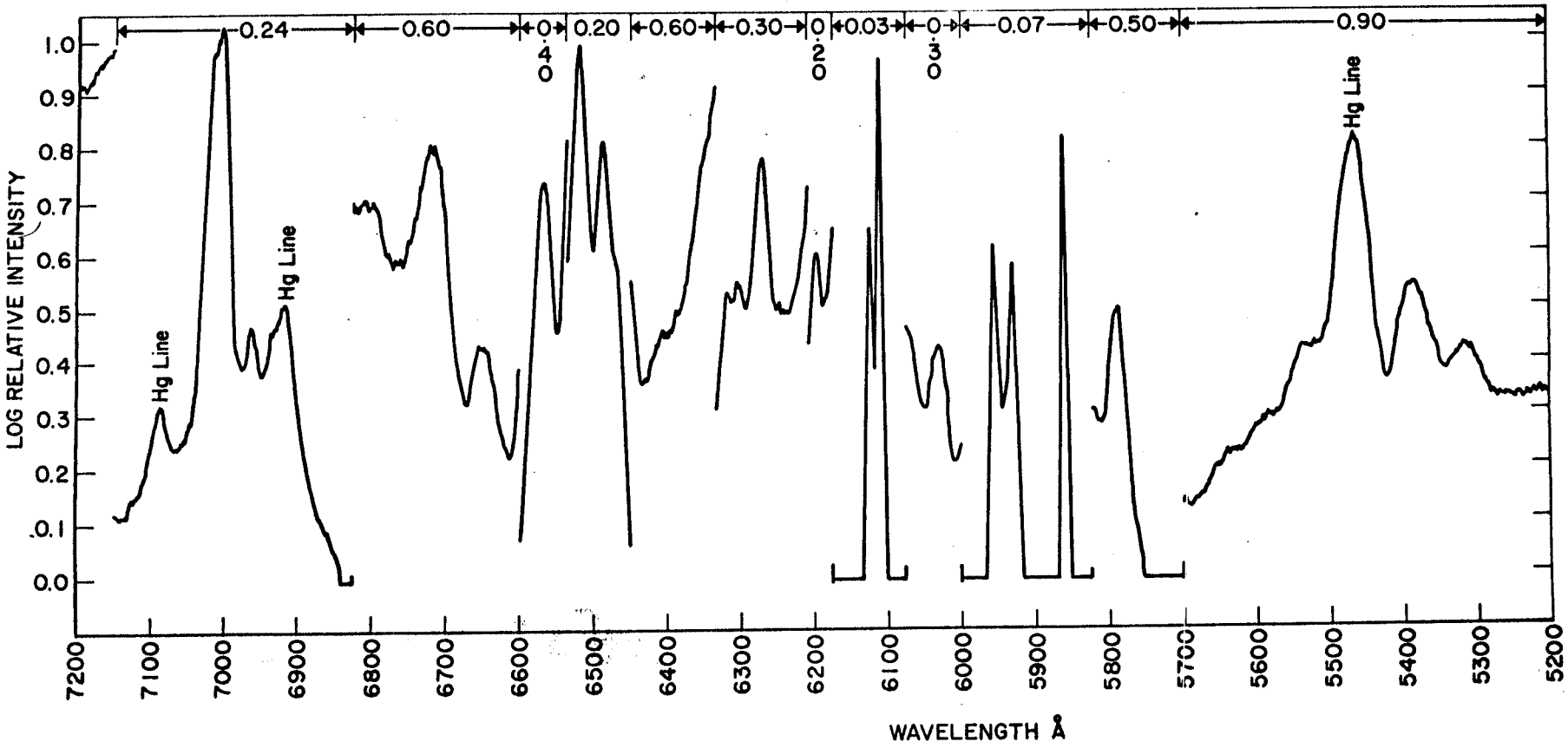


FIGURE 3 (d). Fluorescence spectra of microcrystalline Eu chelates at 77°K (d) EuT_3Dipy

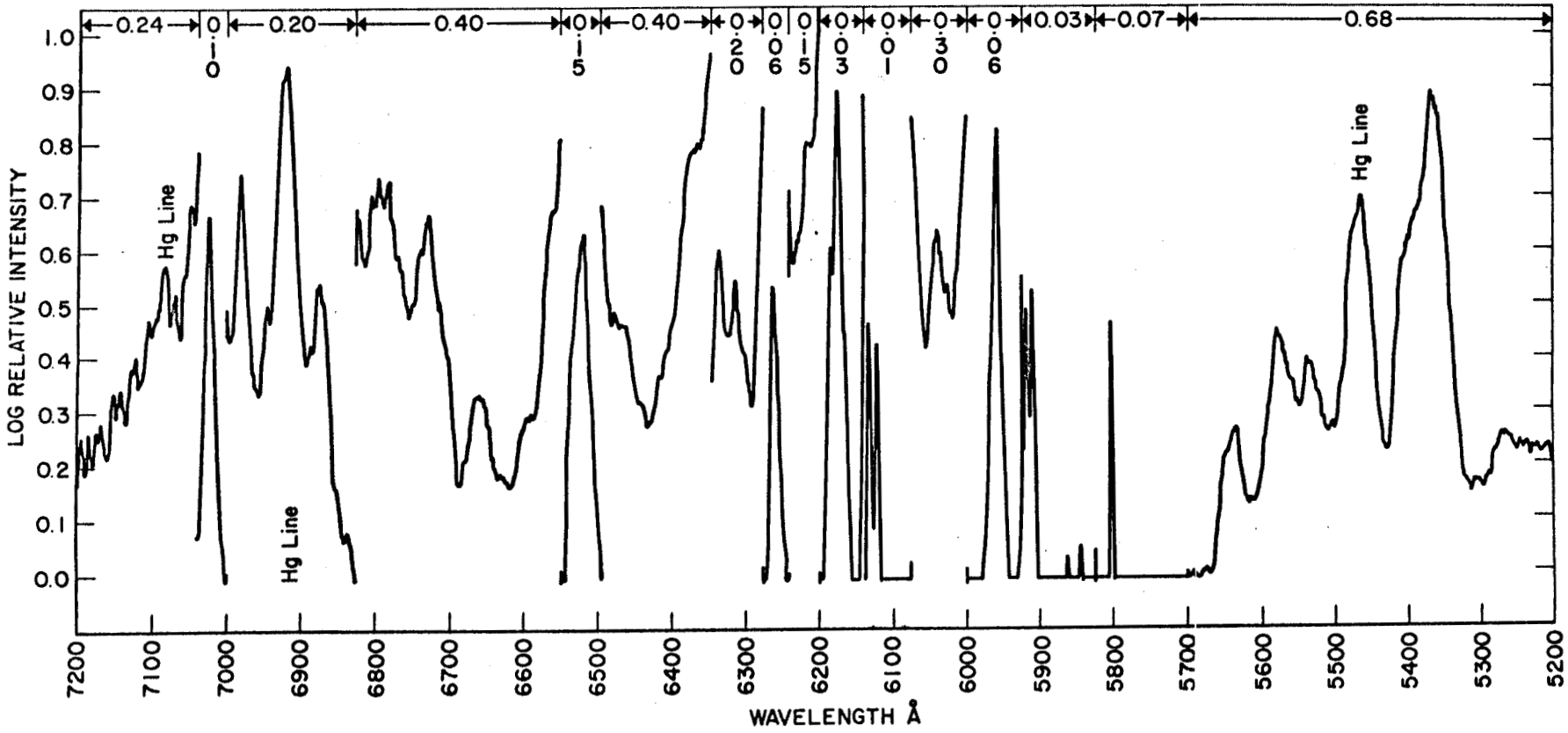


FIGURE 3 (e). Fluorescence spectra of microcrystalline Eu chelates at 77°K (e) EuT_3Phen. (The slit width in mm is given at the top)

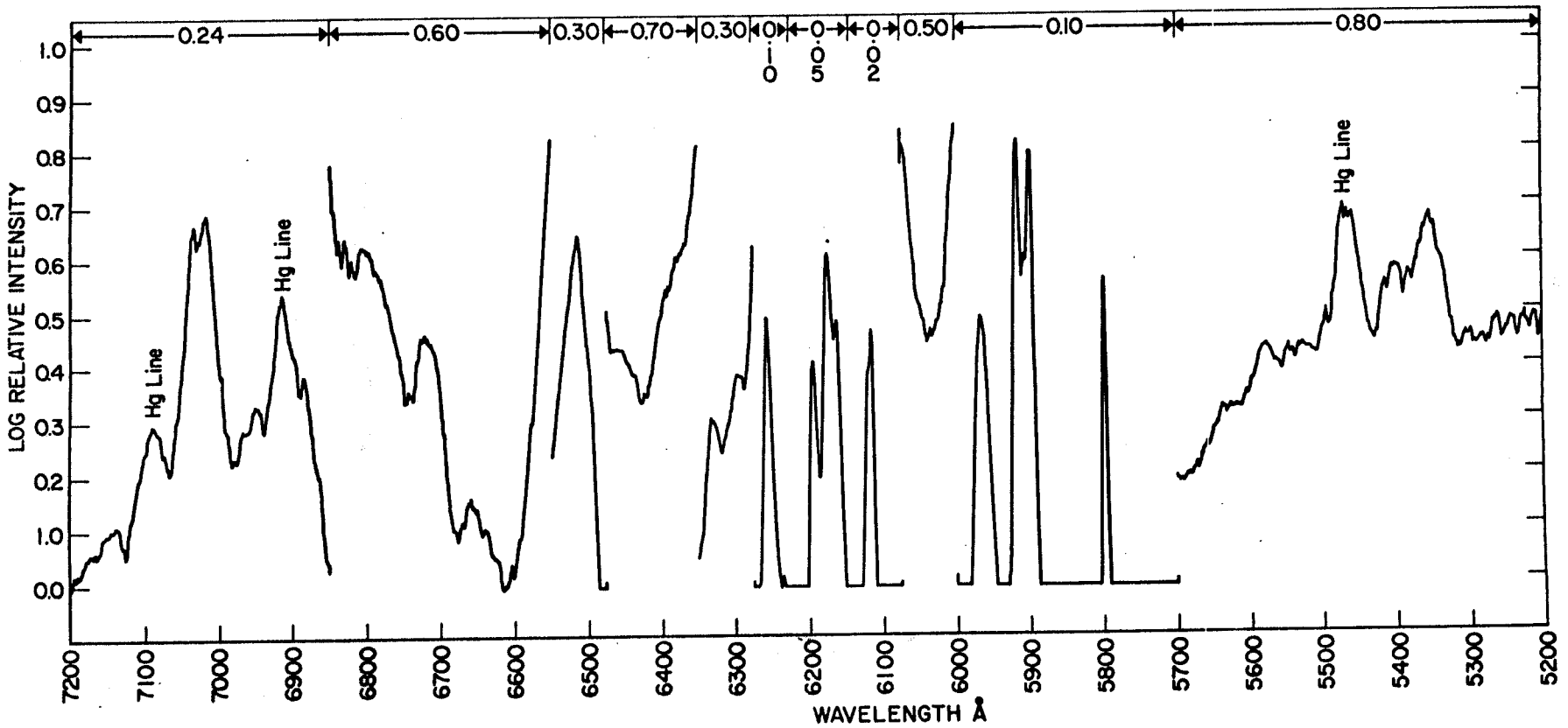


FIGURE 4 (f). Fluorescence spectra of microcrystalline Eu chelates at 77°K. (f) EuD_3.

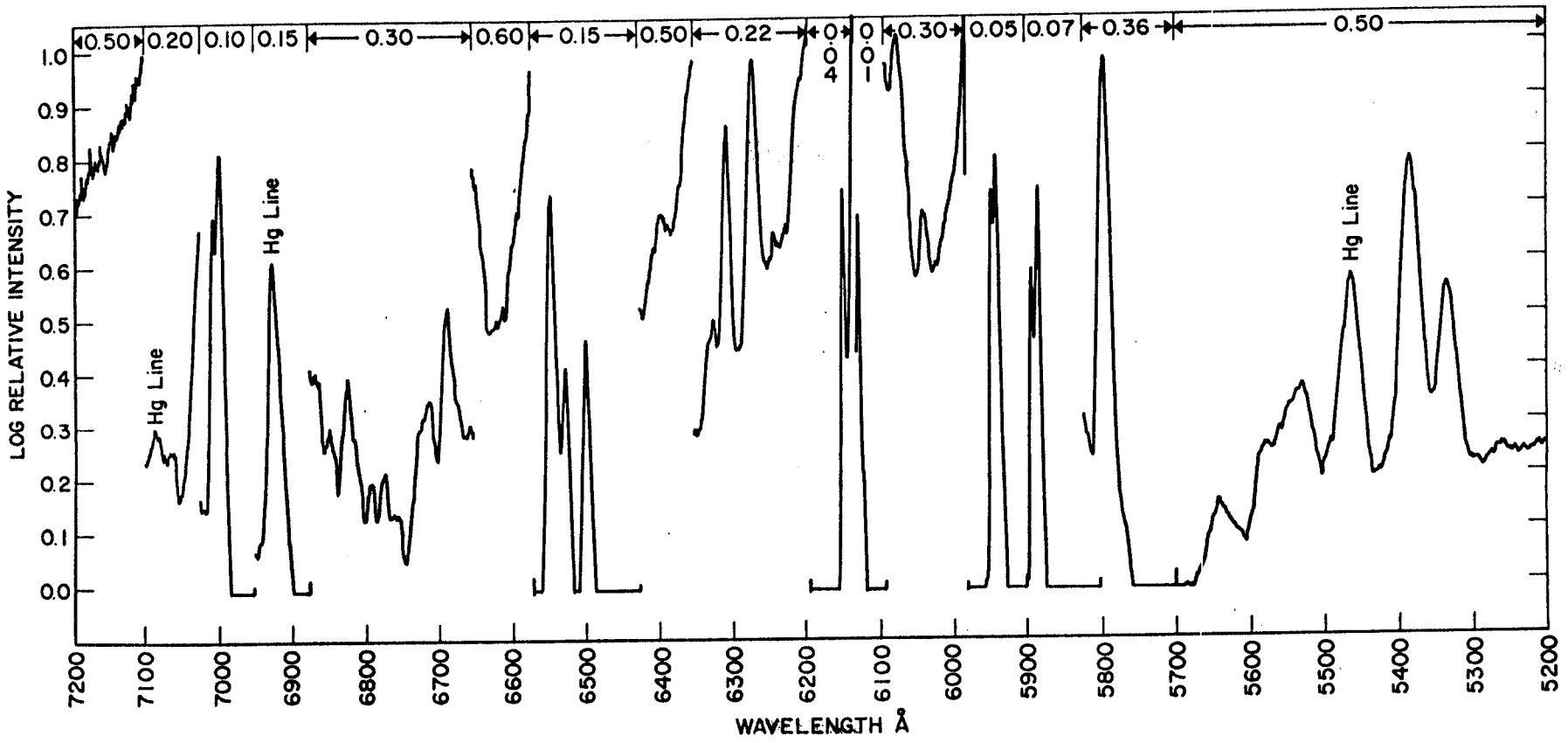


FIGURE 4 (g) Fluroescence spectra of microcrystalline Eu chelates at 77°K.(g) EuD_3A

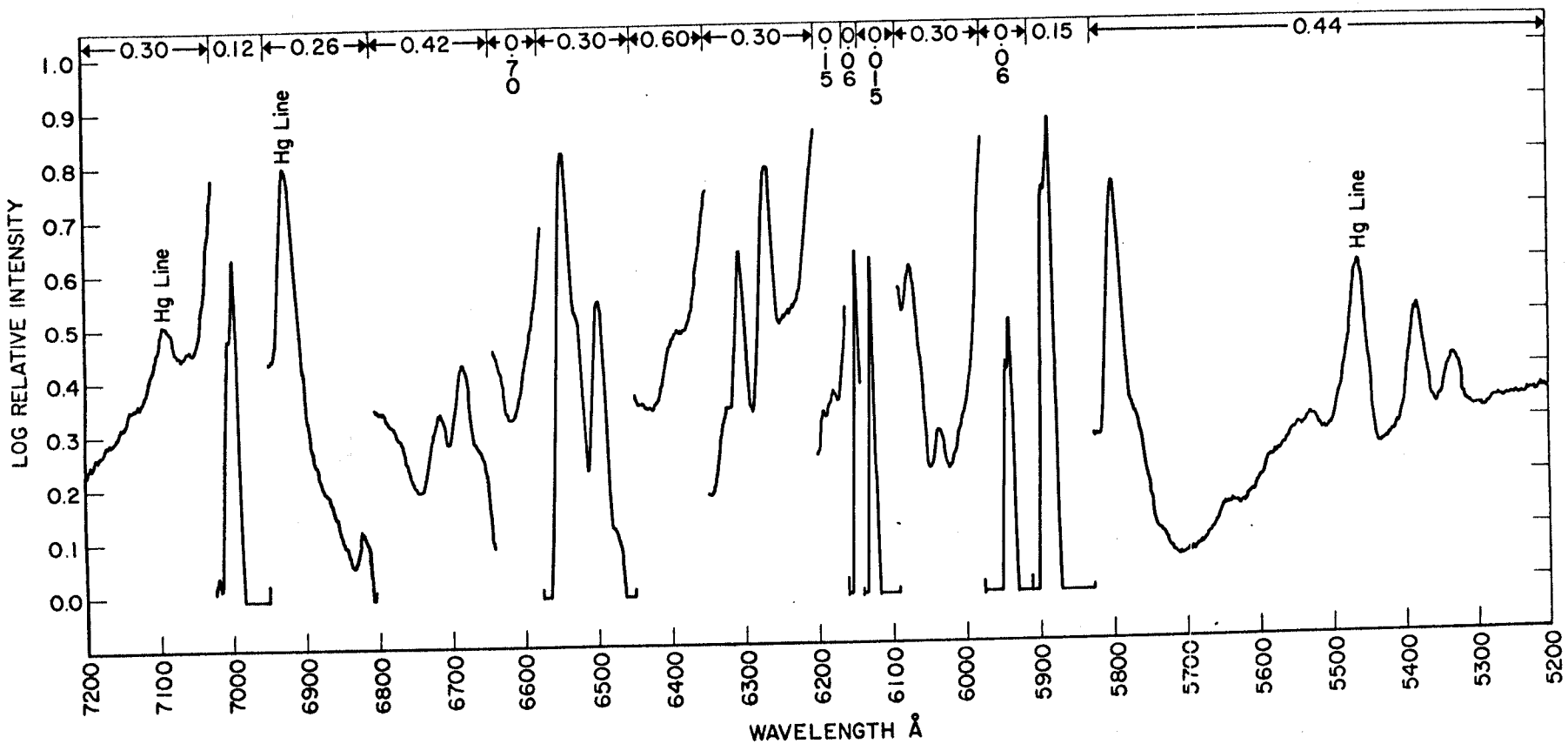


FIGURE 4 (h) Fluorescence spectra of microcrystalline Eu chelates at 77°K (h) EuD_4P

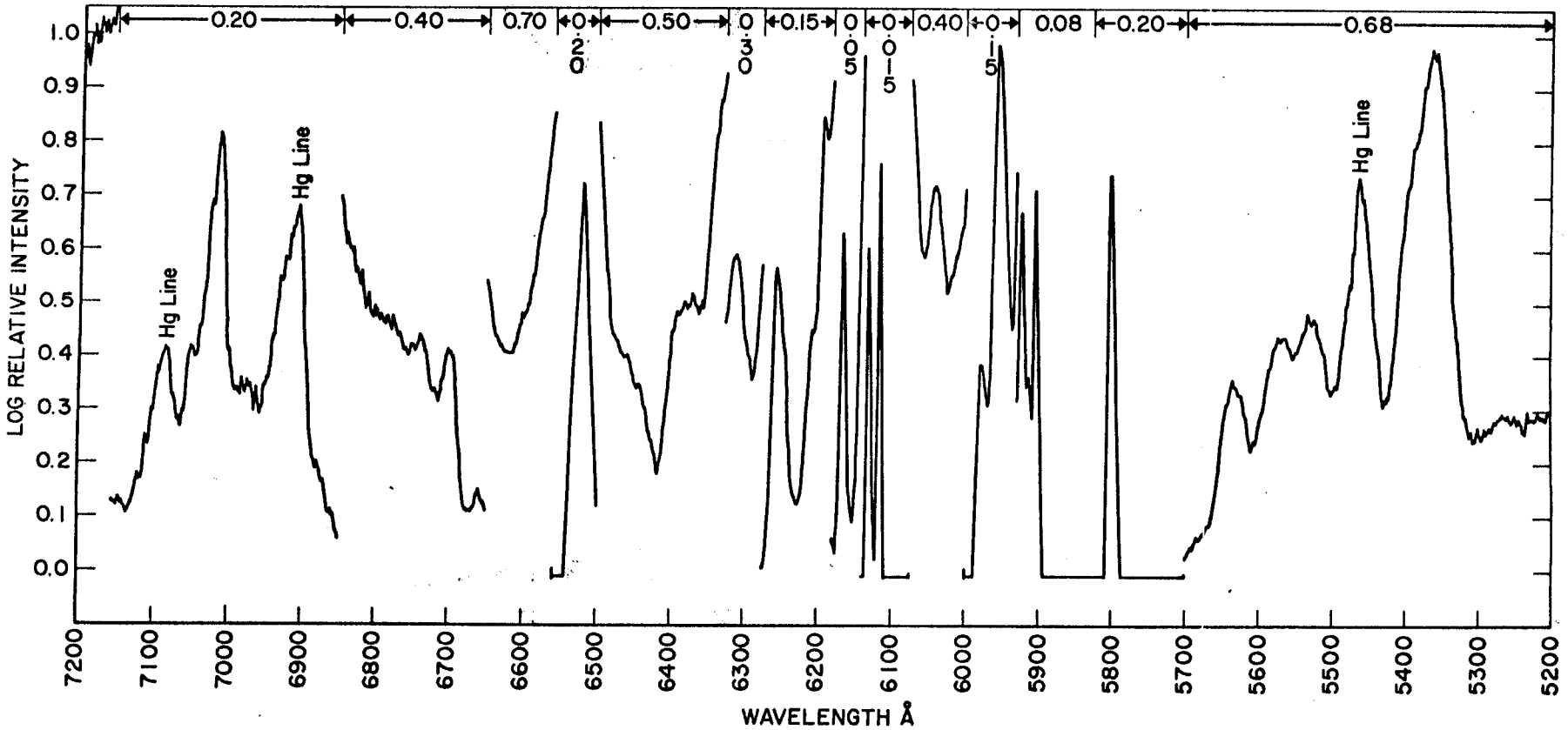


FIGURE 4 (i) Fluorescence spectra of microcrystalline Eu chelates at 77°K (i) EuD_3Dipy

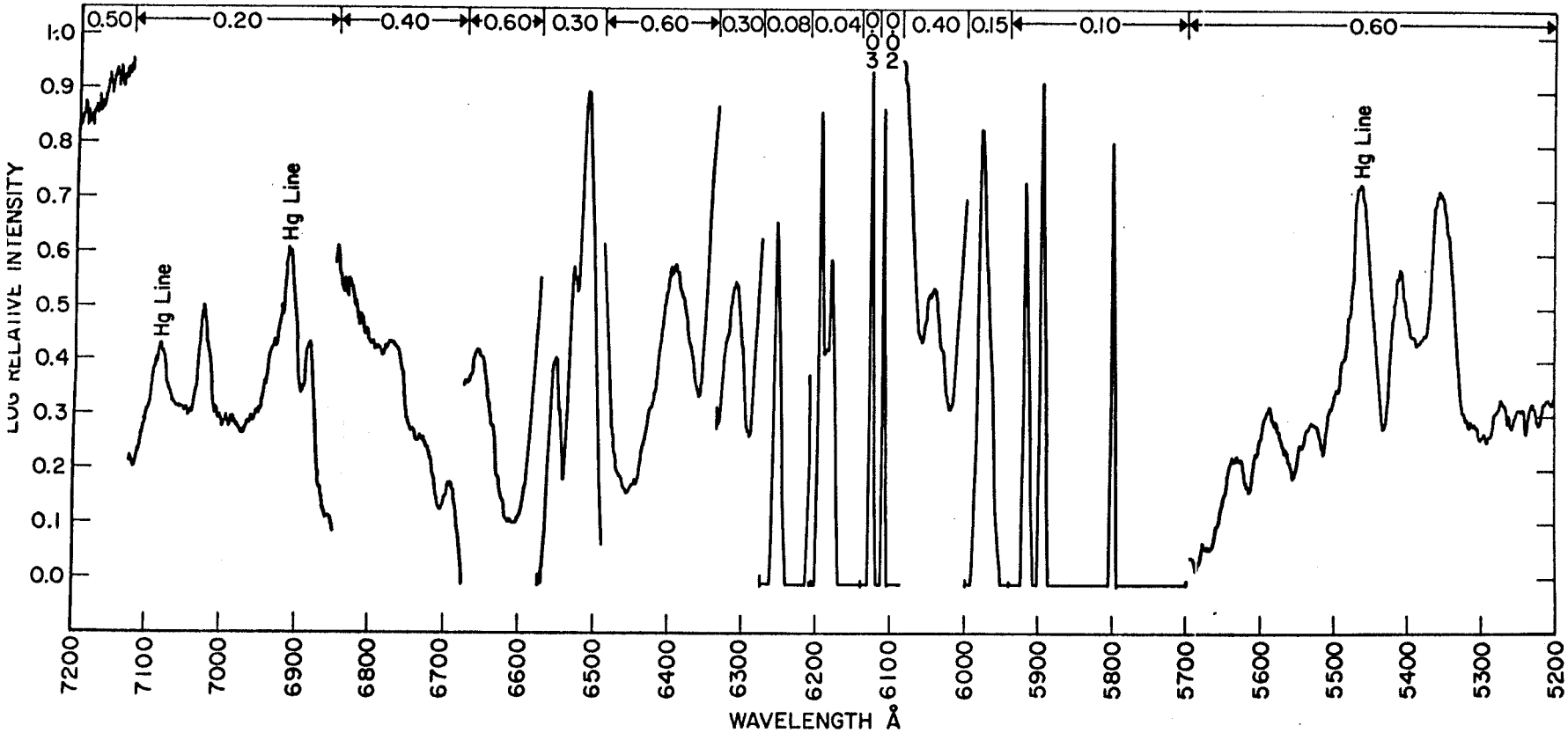


FIGURE 4 (j) Fluorescence spectra of microcrystalline Eu chelates at 77°K. (j) EuD_3Phen.

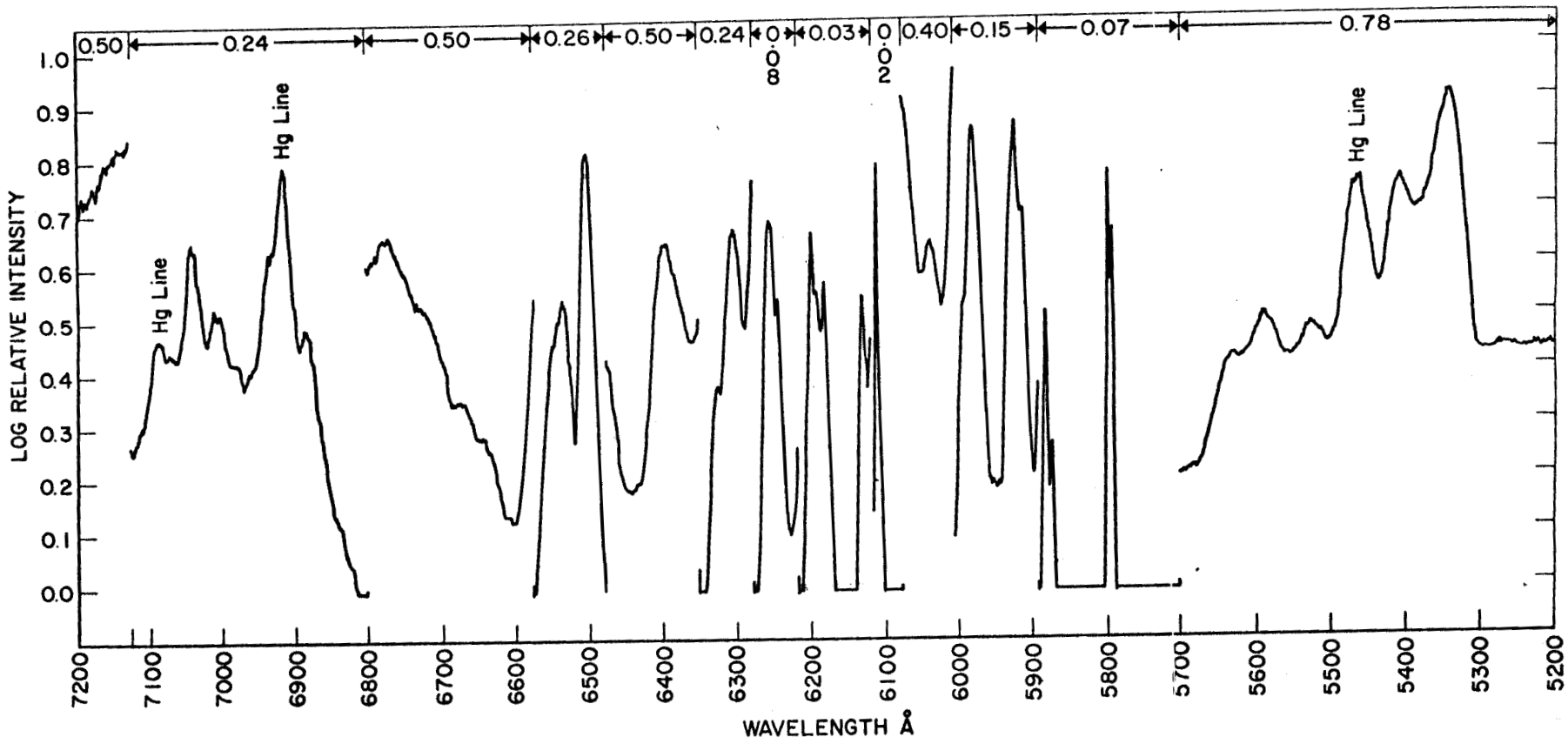


FIGURE 5 (k). Fluorescence spectra of microcrystalline Eu chelates at 77°K. (k) EuB_3

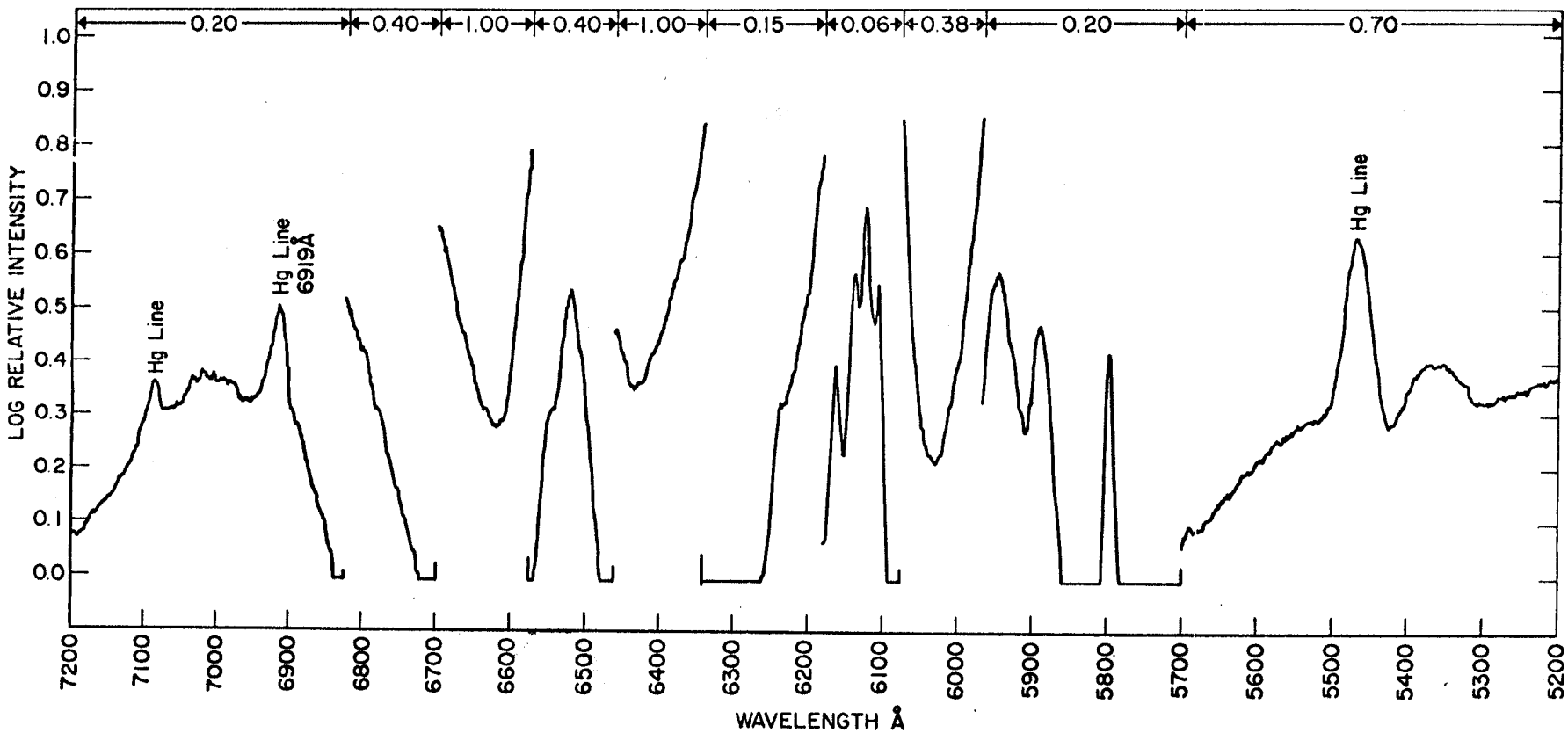


FIGURE 5 (1) Fluorescence spectra of microcrystalline Eu chelates at 77°K.(1) EuB_3A

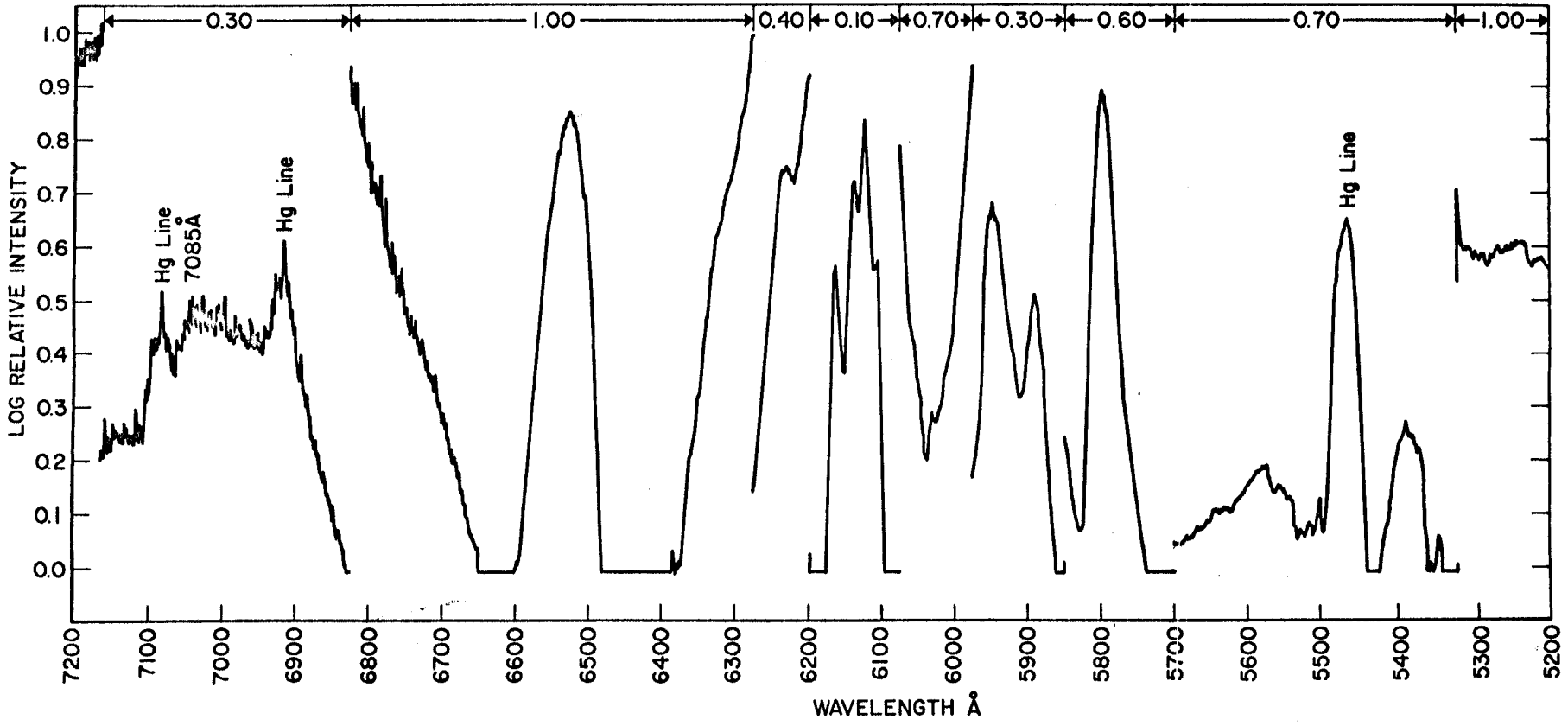


FIGURE 5 (m). Fluorescence spectra of microcrystalline Eu chelates at 77°K. (m) EuB_4P

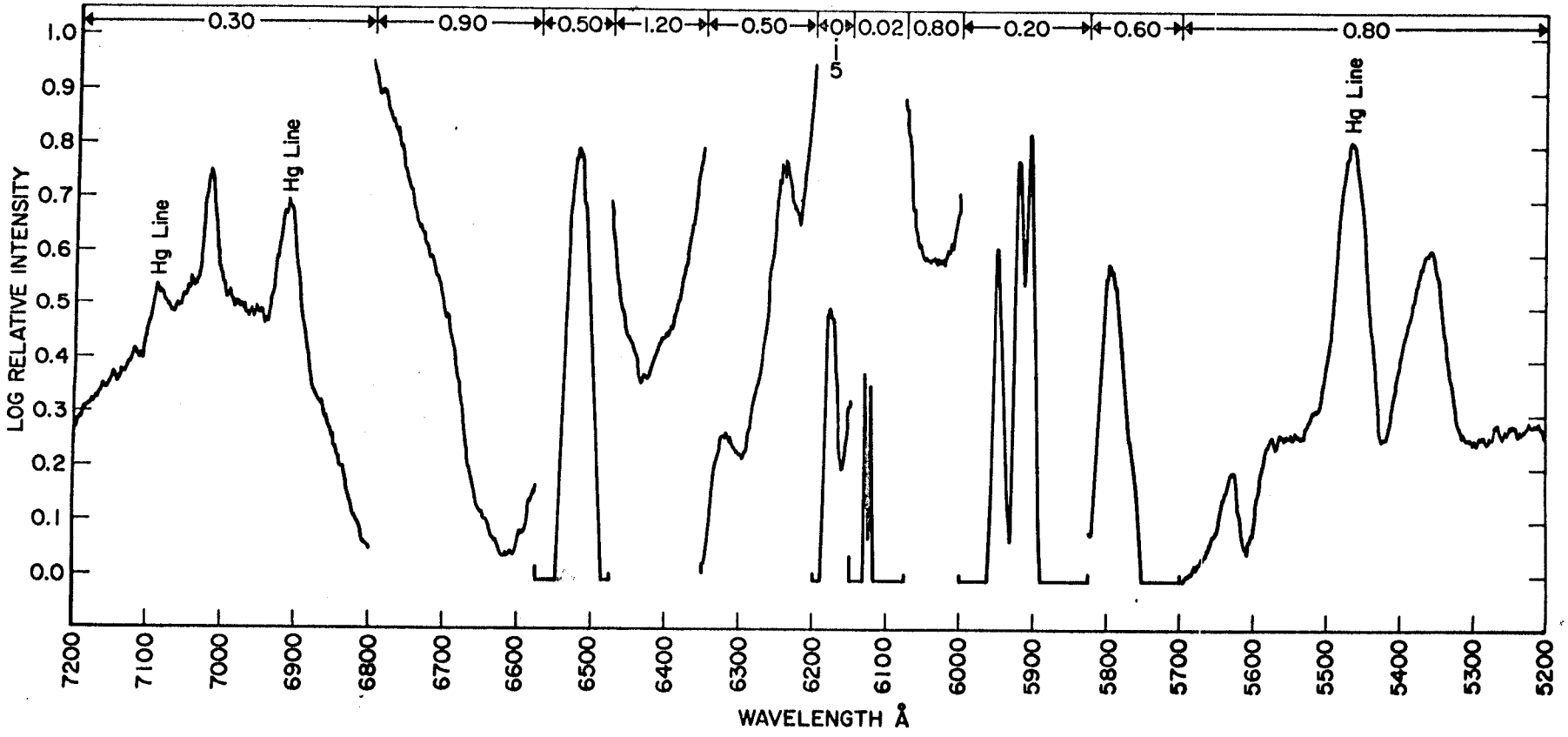


FIGURE 5 (n) Fluorescence spectra of microcrystalline Eu chelates at 77°K. (n) EuB_3Dipy

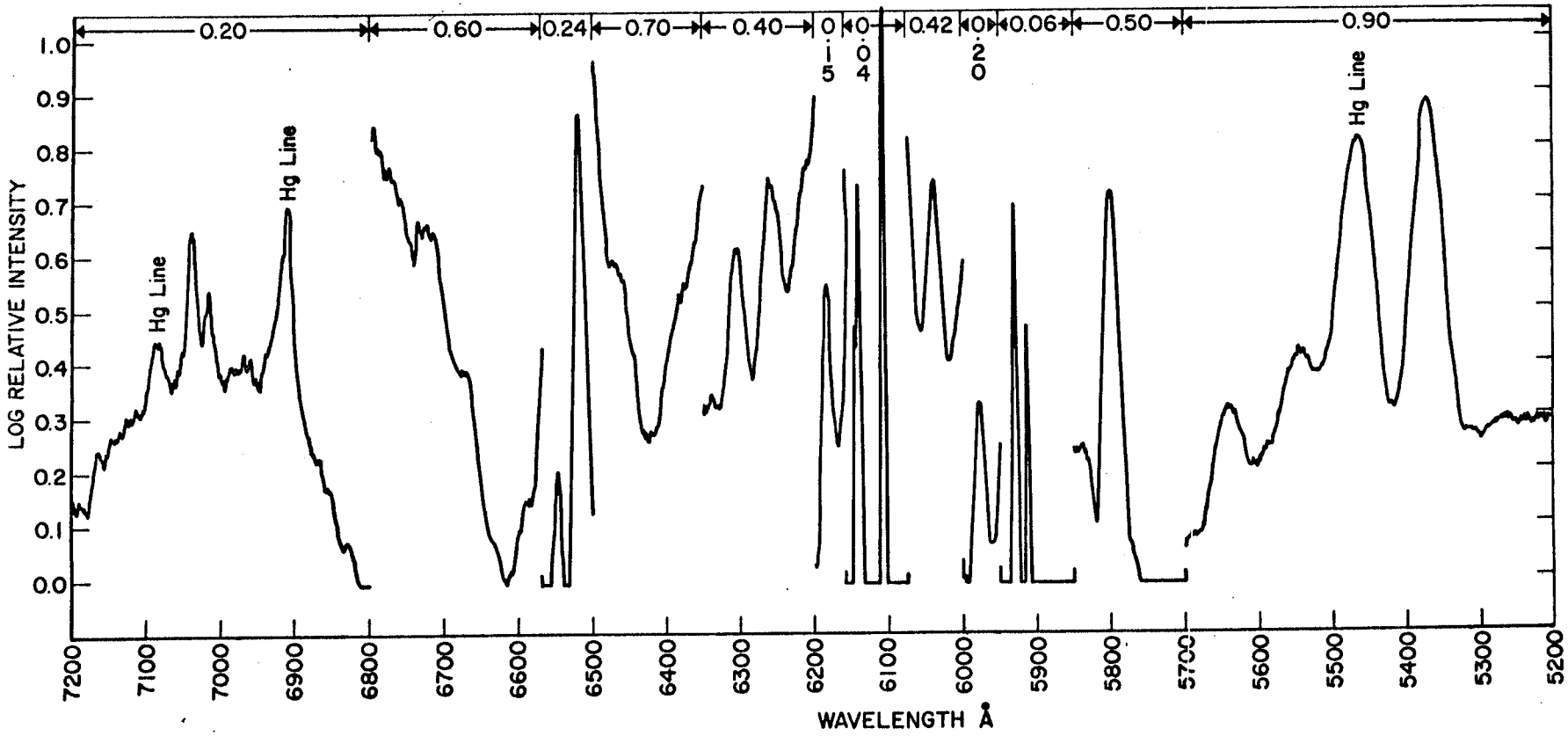


FIGURE 5 (o) Fluorescence spectra of microcrystalline Eu chelates at 77°K (o) EuB_3Phen.

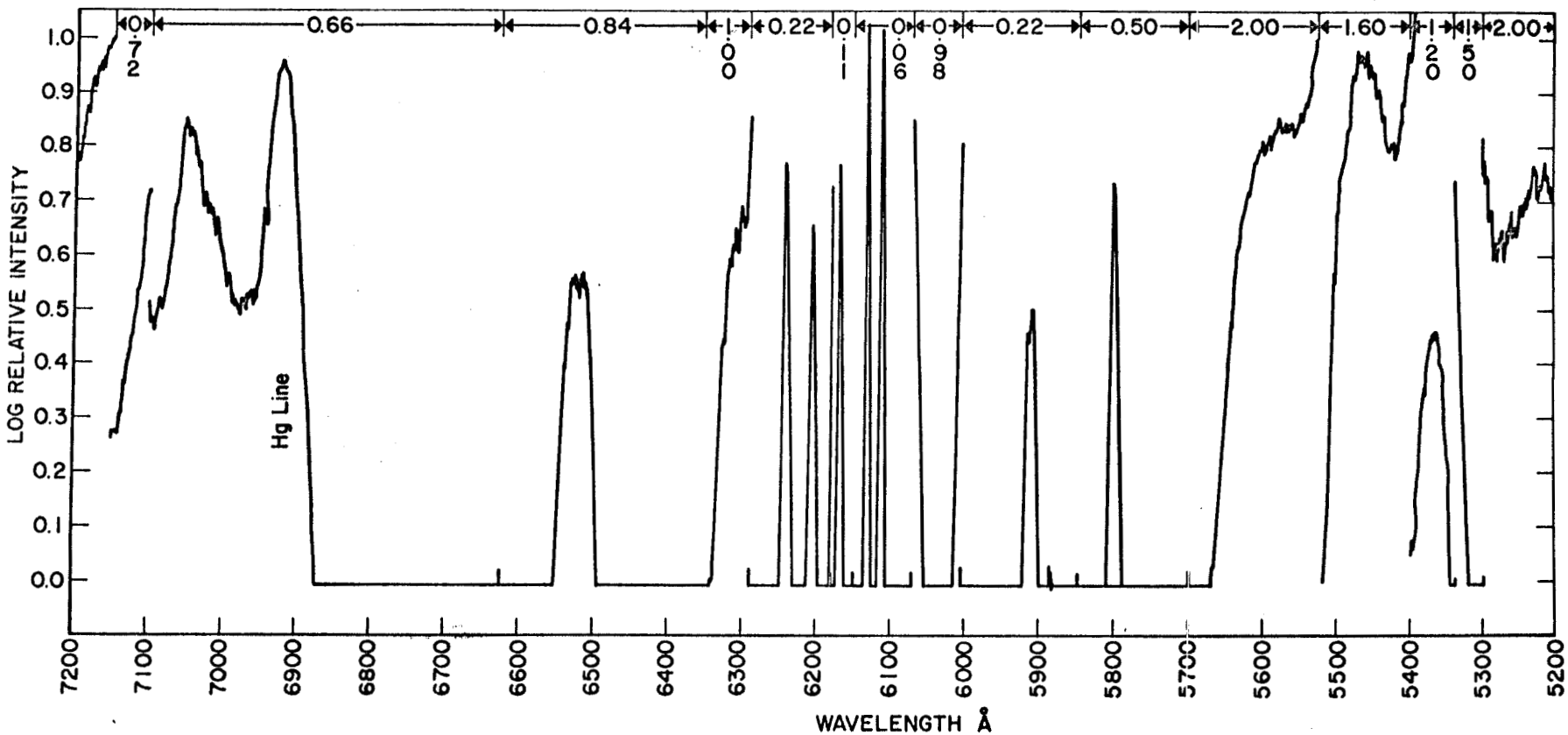


FIGURE 6 (p) Fluorescence spectra of microcrystalline Eu chelates at 77°K (p) EuDipy

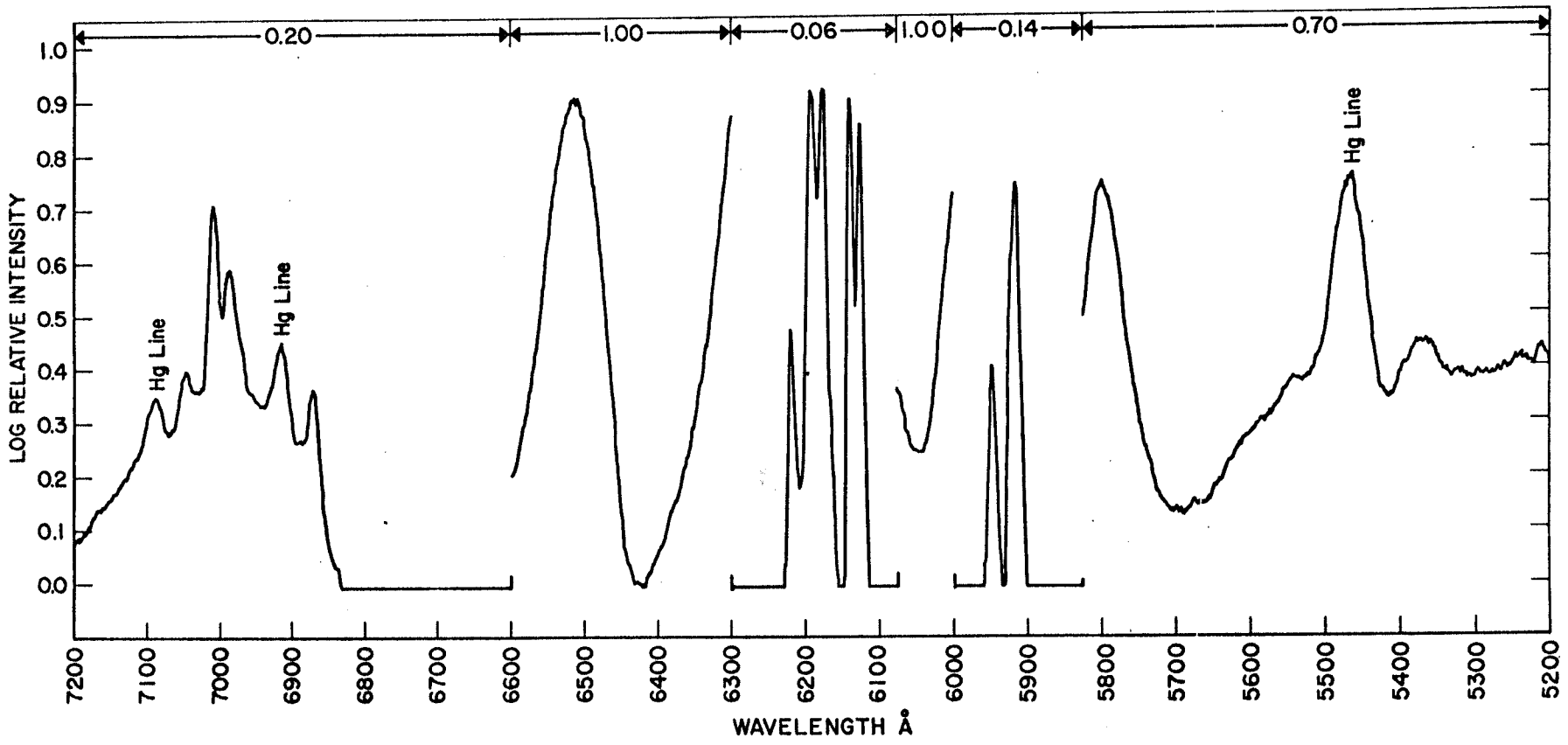


FIGURE 6 (q). Fluorescence spectra of microcrystalline Eu chelates at 77°K. (q) EuPhen.

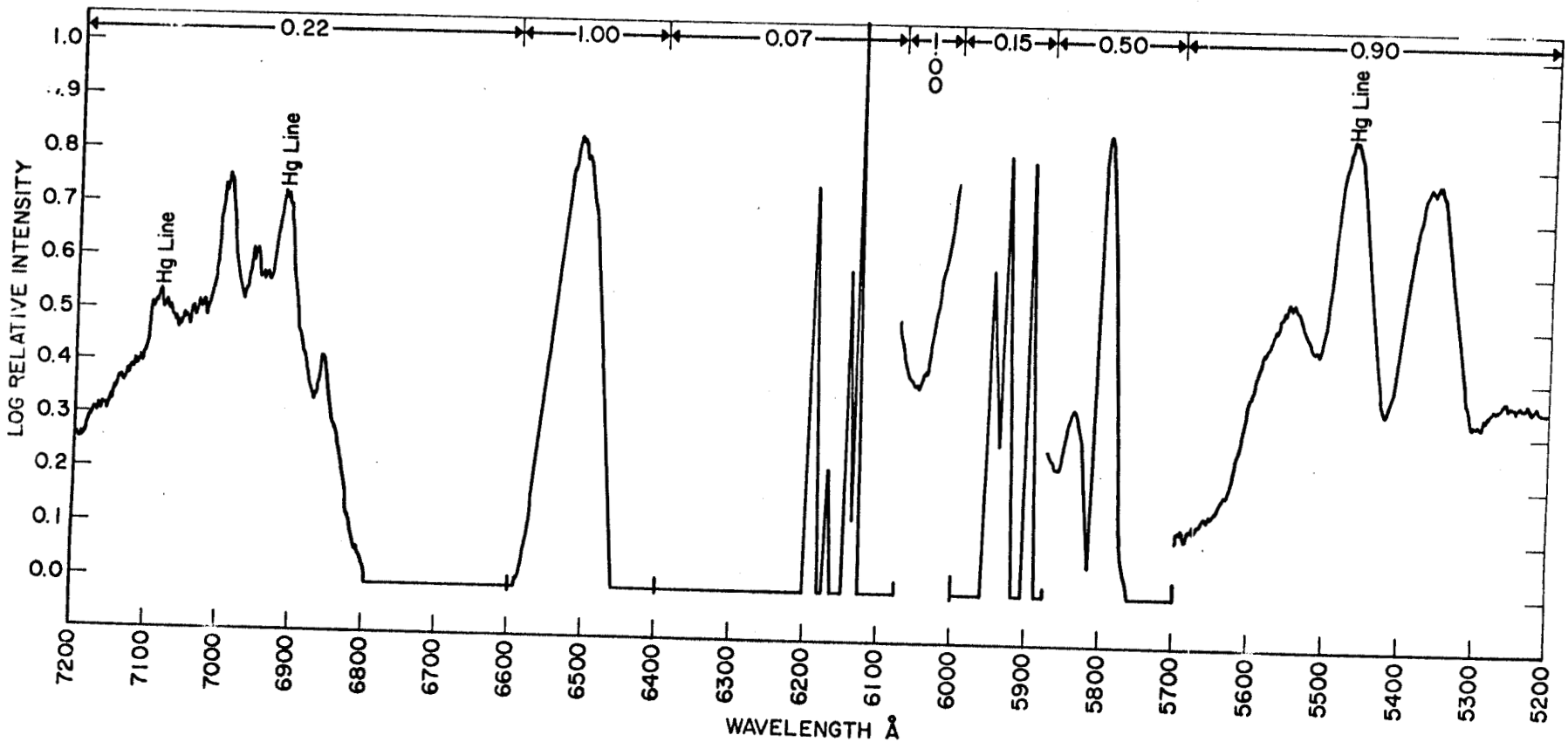


FIGURE 7. Absorption spectrum of EuT_3 10^{-5}M in DMF, 10 cm path, 298°K